Aalto University
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Technology

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Degree Programme of Chemical Technology

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ROUGHER FLOTATION OPTIMIZATION USING RESPONSE SURFACE METHODOLOGY

Master's thesis for the degree of Master of Science in Technology

Submitted for inspection on 10th February, 2015.
Espoo, Finland

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Title of thesis Rougher flotation optimization using response surface methodology

Department Process Systems Engineering

Professorship Plant Design **Code of professorship** KE-30

Thesis supervisor Professor Ville Alopaeus

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Date xx.02.2015 **Number of pages** 86 **Language** English

Abstract

The utilization of Response Surface Methodology as a way to model multiple responses of a process while changing multiple variables in one study, and its application for optimization of the process, has been successfully applied in the chemical and mining industries. A small amount of required tests combined with the capability to make predictions from the obtained models make the methodology attractive for the use in several stages of a concentrator plant: from design and sizing of equipment to continuous improvement on mature operations.

This thesis was developed with the aim to evaluate the applicability of Response Surface Methodology as a tool to perform metallurgical process modelling and optimization on site operations. The proposed methodology was selected due to its flexibility in the selection of multiple variables and responses at once, which allowed gathering sufficient data from a total of 20 batch flotation experiments for copper rougher flotation where pH, collector and depressant dosages were varied to provoke changes in the responses of copper recovery and grade, iron and nickel recoveries.

The obtained results were utilized for the generation of four regression models from which contour line and surface plots were generated for an optimization and determination of feasible region by superimposition of contours. The optimal set-points were determined at values for pH of 10.5, collector dosage of 26 g/t and depressant dosage of 65 g/t.

The accuracy of the prediction for the optimal point was assessed with a series of three confirmation tests with such values kept constant. The result for copper recovery was 82.5%, deviating -2.4% from the predicted point. For copper grade the result was 9.16%, deviating +0.56% from prediction. For iron recovery the result was 6.4%, deviating 0.1% from prediction. For nickel recovery the result was 38.8%, with a deviation of +8.4 from the prediction. In comparison to base-case settings, the optimal point represents comparable relative costs of reagents with expected improvement in results with a particular focus on increased copper recovery by 2% on average.

It was concluded that the methodology is worth exploring further in the different stages of process design, commissioning and working processes. It was demonstrated that with as few as 20 tests it was possible to obtain relevant models and their surface plots, which helped to make a decision for the selection of a new optimal, according to process requirements. It is advised that a future expansion in the methodology for future studies would be for the inclusion of variable screening.

Keywords: Copper flotation, Statistical modelling, Response Surface Methodology, Optimization

Preface

This thesis was the result of the unconditional support provided by Outotec and its team of professionals and my professor Ville Alopaeus from Aalto University, who were always keen on providing support and guidance through its realization. The work took place between January and October of 2014 in Outotec offices in Espoo, as well as Outotec Research Center in Pori, Finland.

I would like to acknowledge all Operation and Maintenance personnel, who were fundamental in helping me to understand the intricate aspects of the business for which my work was meant to support. For the opportunity provided to propose this thesis' topic and the freedom granted for working on a subject that helped me broaden my understanding of Chemical Engineering.

I want to give credit to my colleagues at ORC, starting by my Instructor, M.Sc. Juha Saari, who always patiently helped me channel my ideas and provided valuable insight on the experimental steps and interpretation of results with his proven experience in the industry. Equally important was the contributions of M.Sc. Antti Mankinen and M.Sc. Lauri Veki, who helped me through my experiments and had a positive influence for this work in numerous ways.

Lastly, this work is dedicated to my family and friends in Mexico and Finland, who have always been an important driver and inspiration in my constant pursuit for self-improvement and life. Without them, this adventure in Finland would have never been possible, nor any of the future challenges to be taken.

Arturo Salazar Martinez

January, 2015

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List of symbols and abbreviations

ANOVA	Analysis of Variance
C	Concentrate
CCD	Central Composite Design
CI	Confidence Interval
CMC	Carboxymethyl-cellulose
D_b	Bubble diameter
EDTA	Ethylenediamine tetra acetic acid
Eh	Electric potential
F	Feed
ICP	Inductively Coupled Plasma
IPETC	Isopropyl Ether Thionocarbonate
K	Potassium
k	Flotation rate constant
kg	Kilogram
KPI	Key Performance Indicator
l	Liter
m^3	Cubic meters
Me^+	Metal ion
mm	Millimeter
Na	Sodium
OH^-	Hydroxyl ion
P_{80}	80% passing particle size
PAX	Potassium Amyl Xanthate
pH	Hydrogen potential
RSM	Response Surface Methodology
SE	Standard Error
SX-EW	Solvent Extraction- Electro Winning
T	Tails
TETA	Triethylenetetramine
TI	Tolerance Interval
W	Weight mass
µm	Micron

1 INTRODUCTION

The Minerals Processing industry currently faces a series of challenges such as declining ore grades, increases in the costs of energy sources, water availability, tighter environmental regulations, market volatility and rising prices for reagents and consumables. The existence of the aforementioned factors arise the need for mining companies to study their operations, such as froth flotation of copper, in a way that allows experimenters to isolate significant factors to their process Key Performance Indicators (KPIs) in order to obtain the necessary data for model creation and optimization.

From a process systems engineering perspective, the flotation process can be seen as a system that aims to produce a mineral concentrate that meets requirements for market or subsequent operations while utilizing the least amount of inputs in a profitable manner.

This thesis creates a case study of a copper concentrator in order to evaluate the potential of adapting Response Surface Methodology (RSM) modeling and optimization techniques to diverse clients of the sponsoring company. RSM provides a set of statistical tools for experimental trial design and data analysis that allows to model complex engineering systems by the use of regression methods. These models are obtained after the least amount of experiments needed for the purpose of their optimization, making RSM a potential economical way of generating important information for metallurgical operations.

The responses to be modeled and optimized are, in order of importance, copper recovery, iron recovery, copper grade and nickel recovery. The factors that were determined to be subject to the study were selected by experience of the

customer's site staff and include pH levels, collector and depressant dosage in the rougher flotation part of the concentrator.

The work contains a literature review that will provide the reader with sufficient background in froth flotation of copper ores, followed by an explanation of RSM with reference cases of the chemical and mining industries where it has been applied successfully.

The results are divided into two sections. The first section consists of a standard evaluation of the twenty experiments is provided in order to determine its adherence to the theoretical principles provided. The second section will cover the application of RSM with the data collected to model the four responses, selection of the best fitting models and the optimization procedure.

It is important to state that the results from this study are not meant to be implemented in the operations of the customer, but rather serve as the seminal work for adapting the methodology to a wider set of metallurgical processes in the future. The methodology is intended to serve as a supporting tool for cases ranging from green-field process design to operation and maintenance contracts of any of the process technologies covered by Outotec service organization.

Flotation is one of the most widely used beneficiation processes for copper extraction. Feedstock mineral compositions, proper physicochemical characterization of the ore properties, and the isolation of the most influential process variables that affect flotation performance are of high importance for any mining operation in most of the processing stages. (Drzymała 2007; Fuerstenau et al., 2007; Napier-Munn and Wills, 2011)

This chapter will provide a theoretical framework to support the identification of variables that are critical to the copper flotation system performance. A selected number of these variables will be then selected for the development of a statistical model for prediction and optimization of copper recovery and grade from a copper-nickel ore.

2 Minerals and ores

Minerals are naturally formed materials, mostly by geological or cosmic processes, that present strictly defined chemical composition, internal structure and physicochemical properties which ultimately determine the best processing method for obtaining, e.g., base metals such as copper from economically viable ores.

There are different classifications for minerals. Drzymała (2007) presents a classification of minerals based on chemical composition and it is presented as follows:

- Native elements, alloys and intermetallic compounds
- Carbides, nitrides, phosphides and silicides
- Sulphides and related minerals

- Halides
- Oxides and hydroxides
- Salts of oxy-acids (nitrates, iodates, carbonates, selenates, tellurates, borates, sulfates, chromates, molybdates, tungstates, phosphates, arsenates, antimonates, vanadates, uranates, geramanates, silicates and aluminosilicates)
- Ammonium minerals
- Organic compounds

There is an important distinction to be made between minerals and ores. Ores relate exclusively to material that has been extracted from the earth's crust and that has been determined to present economic potential after undergoing an extractive metallurgical process, such as flotation (Lane, 1988). Since minerals containing elements of interest, such as metals, are present in the earth's crust in a disseminated way, a metal-bearing ore therefore usually contains multiple types of minerals.

Furthermore, ores can be classified according to the metal of interest, such as cuprous or ferrous ores, the main chemical group that gives its characteristics such as oxidized or sulphides, the nature of their gangue materials, such as siliceous or clays; or even complex ores, if more than one metal of economic interest is present, which could arise the need for more complex processes for their separation and beneficiation. (Napier-Munn and Wills, 2011)

This thesis will solely focus on the flotation of copper-bearing minerals as well as the commonly associating minerals, such as nickel-bearing ones, that are present in the studied sample, which belongs to an orthomagmatic mafic-ultramafic copper-nickel ore body.

2.1 Copper minerals

There are approximately 170 identified copper minerals. However, only about eleven of these minerals are considered viable for their processing and extraction of copper (Bulatovic, 2007). Two main distinctions can be made in order to classify copper minerals: sulphides and oxide minerals. In terms of their responsiveness to froth flotation, the most suitable minerals are the sulphide kind, while oxides can be successfully treated primarily via acid leaching and a solvent extraction and electro-winning process (SX-EW) (King et al, 2011).

However, due to the nature of the mineral forming processes, a specific type of copper mineral seldom occurs in isolation, but rather undergoes a series of reactions driven by geological and meteorological processes that result in the formation of a variety of copper containing sulphides and oxides along with gangue minerals that determine the complexity of the ore body (Robb, 2009). Table 1 presents a list of the commercial copper ores with the theoretical copper content and common associated minerals.

Most of the presented copper minerals occur in porphyry ore deposits derived from magmatic arc formations (Wilkinson, 2013). Other important types of deposits include sedimentary, shale-hosted deposits and supergene alteration zones and shale (Dill, 2010). The ore studied in this thesis belongs to the orthomagmatic mafic-ultramafic type, which contains highly disseminated sulphide minerals (up to 5%) with an average copper grade of 0.41% and nickel grade of 0.3%. The main minerals found in the ore are pyrrhotite, chalcopyrite and pentlandite, which is a nickel-bearing mineral of formula $(Fe,Ni)_9S_8$. The ore presents characteristics similar to the ones presented by Malehmir et Al. (2014). The main metals of interest, therefore, are copper and nickel, with focus of rejection of as much iron as possible from the final concentrate product.

Table 1. Principal copper minerals found in commercial ores. Different processing methods are utilized for sulphides and oxides. As a rule of thumb, sulphides undergo flotation and oxides are processed via acid leaching (Napier-Munn and Wills, 2011).

Ore minerals	Formula	% Cu	Occurrence/associations
Chalcopyrite	$CuFeS_2$	34.6	Main ore mineral. Most often in veins with other sulphides, such as galena, sphalerite, pyrrhotite, pyrite, and also cassiterite. Common gangue minerals are quartz, calcite, and dolomite. Disseminated with bornite and pyrite in porphyry copper deposits.
Chalcocite	Cu_2S	79.8	Often associated with cuprite and native copper.
Bornite	Cu_5FeS_4	63.3	Associates with chalcopyrite and chalcocite in veins.
Covellite	CuS	66.5	Sometimes as primary sulphide in veins, but more commonly as secondary sulphide with chalcopyrite, chalcocite, and bornite.
Cuprite	Cu_2O	88.8	Found in oxidized zone of deposits, with malachite, azurite, and chalcocite.
Malachite	$CuCo_3$-$Cu(OH)_2$	57.5	Frequently associated with azurite, native copper, and cuprite in oxidized zone.
Native	Cu	100	Occurs in small amounts with other copper minerals.
Tennantite	Cu_8As2S_7	57.7	Tennantite and tetrahedrite found in veins with silver, copper, lead, and zinc minerals.
Tetrahedrite	$4Cu_2S{\cdot}Sb_2S_3$	52.1	Tetrahedrite more widespread and common in lead-silver veins.
Azurite	$2CuCO_3{\cdot}Cu(OH)_2$	55	Occurs in oxidized zone. Not as widespread as malachite.
Enargite	$Cu_3A_5S_4$	48.4	Associates with chalcocite, bornite, covellite, pyrite, sphalerite, tetrahedrite, baryte, and quartz in near-surface deposits.

3 Process theory

The transition from a mineable ore resource to a final copper concentrate is only possible through the extraction of the ore from the mine pit and its further processing in a copper concentrator. A copper concentration process can be considered as an engineering system consisting of a varying number of subsystems (unit and process operations). These operations provide the inputs to the froth flotation process, which at its own generates major inputs for the later smelting and refining stages. (Drzymała 2007; Fuerstenau et al., 2007; Napier-Munn and Wills, 2011)

The copper froth flotation process is based on the attachment of hydrophobic mineral particles of different affinities to air bubbles. This process is controlled by a number of chemical, operating and process equipment related variables. Figure 1 presents a few examples on the three main groups of variables related to the flotation process. The froth phase is collected and referred to as the copper concentrate, which contains a higher grade of copper relative to the feed material and has been stripped from gangue minerals, which reports to the underflow from the flotation cell banks and is known as the tailings. (Klimpel, 1995)

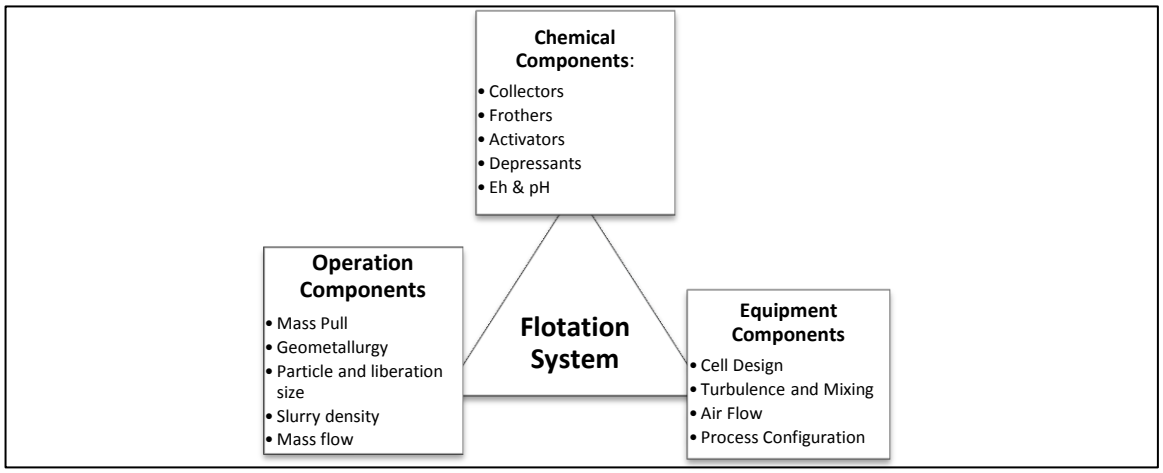

Figure 1. Schematic presentation of a flotation system including examples of the three major components: chemical, operational and equipment related. Adapted from Klimpel (1995).

The following sections will explain in further detail the effects of the formerly presented variables into the flotation system. Even though only three variables were selected for the study, it is important to remember that, depending on the particular case and level of optimization present in the operations, the prioritization of such variables is subject to change and therefore any of these variables could be studied by the methodology.

3.1 Process flow diagram

The basic layout for a concentrator plant includes the comminution (size reduction of the ore), screening, gravimetric concentration, flotation and dewatering circuits.

The comminution circuit receives material and operating inputs, such as ore hardness, feed particle size from blasting or crushing stage, mass flow, power inputs, ball charge, and rotation speed among others. Its material outputs enter the flotation circuit, which operates with the variables outlined in Figure 1 and produces the feed conditions for the dewatering stage. A typical flow diagram of a concentrator plant is presented in Figure 2.

A typical concentrator includes rougher, scavenger and cleaning flotation stages, followed by tails and concentrate dewatering by the use of thickeners and pressure filters for the later and typically tailing ponds for the former. Each of the flotation stages presents different objectives in terms of recovery, grade and type of minerals expected to be separated to their respective concentrate or tail streams.

In the case of this thesis, the first rougher stage is for achieving maximum copper recovery while trying to keep other non-interest metals low on recovery and grade. The cleaning stage is designed to improve the copper grade by lowering gangue and other metals such as nickel by sending them to the tails stream. This stage is aided by the incorporation of regrinding equipment that helps lower the particle size and therefore liberate the copper minerals for performing a more selective flotation in the cleaning cells. Lastly, the scavenger stage, which follows rougher flotation, is a flotation of the recirculated tails to recover any missing copper and improve the process efficiency. (Fuerstenau et al., 2007; Napier-Munn and Wills, 2011)

This thesis covers only a small fraction of the complete flotation plant. The selected stage was the copper rougher flotation section, in which the primary goal was to achieve maximum recovery at the lowest possible reagent dosage and with the lowest possible concentration of nickel and iron in order to create better rougher concentrate quality to lower regrinding inputs as well as reagent needs in subsequent flotation stages.

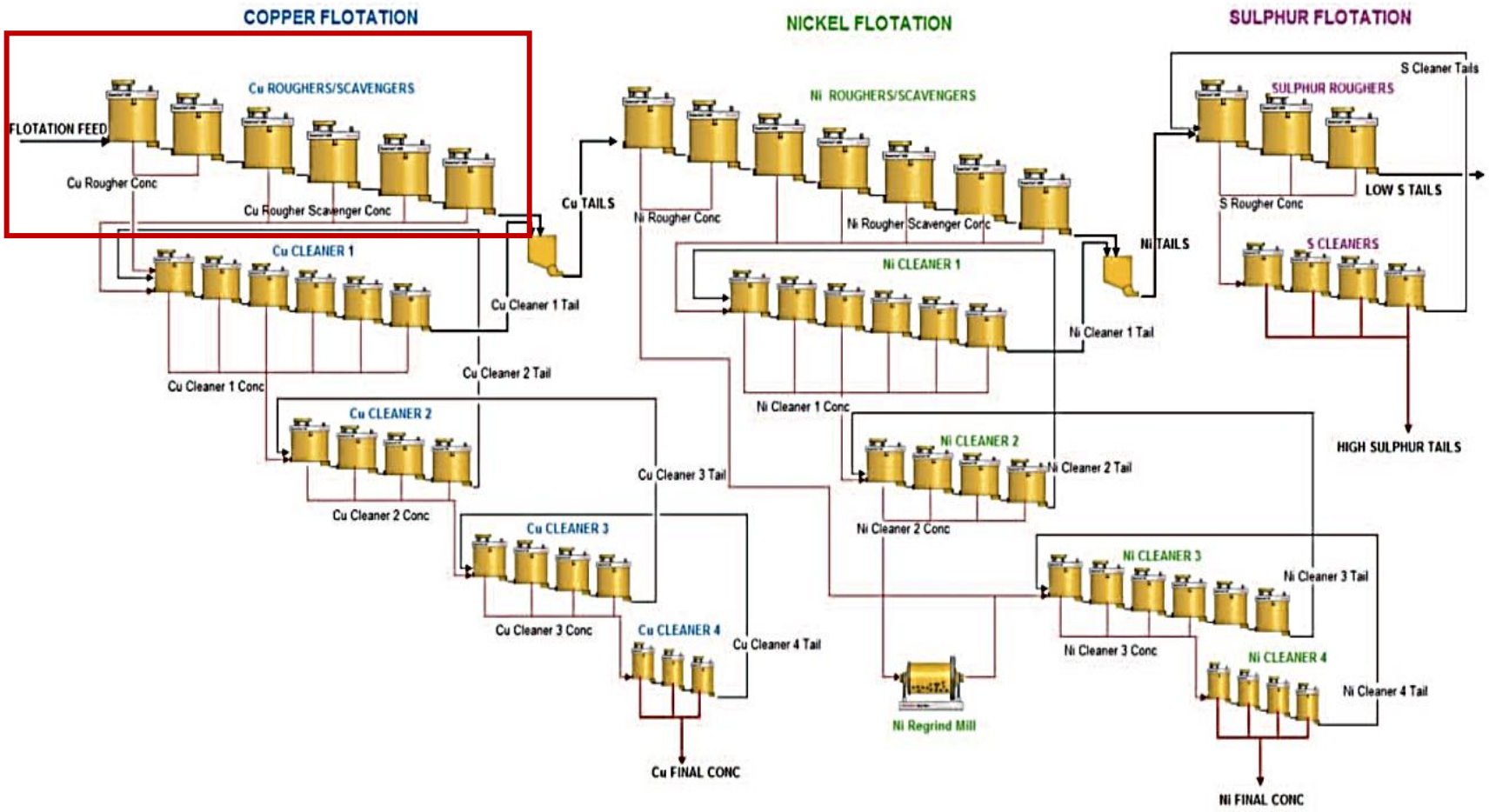

Figure 2. Process Diagram with scope of the study in copper rougher flotation.

3.2 Chemical components

3.2.1 Collectors

Since the vast majority of minerals, including copper ones, are by nature hydrophilic, they need to be rendered hydrophobic through the addition of special reagents denominated as collectors. The most widely utilized collectors for sulphide minerals are the ionizing type. These collectors dissociate in water and absorb chemically to the mineral surface based on chemical affinity (Drzymała, 2007). In the case of copper sulphide minerals, the most widely used collectors are sodium or potassium xanthates, which have a general structure of the form ROCSS-(Me), where R is an organic radical and Me can represent K, Na or H (Bulatovic, 2007). Another type of collectors that is used for copper minerals are dithiophosphates and thionocarbamates, often recommended for chalcopyrite (Fuerstenau et al., 2007).

Depending on the concentration and pH levels, different sulphide minerals behave in faster or slower ways in terms of flotation kinetics, as exemplified by Figure 3. Some minerals, such as pyrite and galena, present improved floatabilities at acidic or near neutral conditions under a specific collector dosage, while chalcopyrite responds better to alkaline conditions. Floating behavior is observed to the left of the line, while non-floating behavior is observed to the right (Bulatovic, 2007; Drzymała, 2007; King et al., 2011). This behavior is then exploited to perform selective flotation by regulating the pH conditions in order to discard, e.g., pyrite minerals in one stage by depression at higher pH ranges without affecting chalcopyrite flotation.

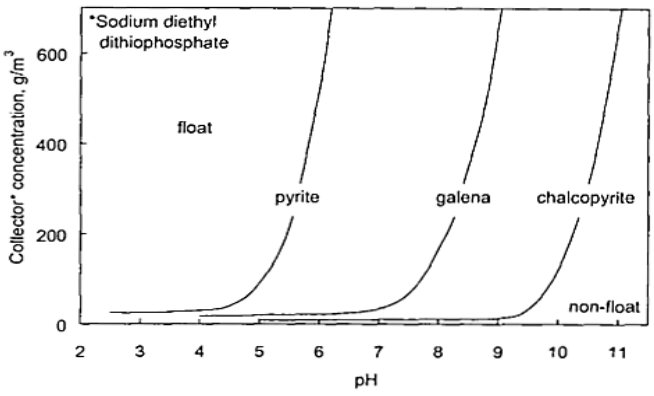

Figure 3. Effect of collector and pH in the flotation of different sulphide minerals (King et al., 2011).

3.2.2 Frothers

The role of frothers in a flotation reagent matrix is to aid the formation of a stable froth phase. The air bubbles in a flotation cell typically form in pairs with diameters averaging 4 mm. The addition of frother, in combination with the design of the air diffuser results in the reduction of bubble coalescence with a more sparsely array with bubble diameters averaging 1 mm, which improves the spatial distribution, stability and surface area for the collection of mineral particles. It has been suggested that the bubble diameter has an inverse first order relationship with the flotation rate constant ($1/D_b$). (Grau et al., 2005; Zhang et al., 2012)

The selection of frother reagents needs to be performed carefully taking into account the different phases by which the bubbles are formed, dispersed, and their motion upwards onto the surface of the froth phase while collecting gangue and valuable mineral particles. The effects on recovery and selectivity are closely related to the mineralogy composition of the slurry as well as the particle size of the ground particles and the pH conditions present in its environment (Bulatovic, 2007). Therefore, the frother blend has to be such that:

- In the presence of clays or slimes, the froth is wet enough so that gangue material does not attach to the bubbles
- Bubbles are not so stable that they do not break after being collected at the top of the cell and can be washed from particles by the launders

- In the presence of pH modifiers and depressants, the frother is able to remain stable enough to withstand the changing conditions found from rougher to cleaning cells.

3.2.3 Promoters

Promoters are specialty collectors that are utilized in cases where selectivity, and thus penalties on trace elements on the final concentrate represent a major issue for a flotation circuit. Some promoters are composed of Isopropyl Ether Thionocarbonate (IPETC), and incorporate special iron sulfide mineral rejection to the collection (which is in a way a special type of depression on non-gangue mineral). Their dosage has to be carefully determined via laboratory studies, since it has shown to create flattening and drying effects on the froth when overdosed. (Day, 2002)

3.2.4 Depressants

The function of depressants is opposite to the one of activators. In principle, a depressant impedes the adsorption of the collector on certain mineral particles that are required to be selectively discarded, such as gangue minerals.

There are several types of depressants. Some pH regulators, such as lime can act as depressants for certain sulphide minerals, such as pyrite. Other types of selective depressants include sodium cyanide, where the CN^- ion dissolves metal species, such as Fe avoiding its contact with the collector. (Bulatovic, 2007)

An important category of depressants for copper flotation is the one of anionic polymers, belonging to the group of organic depressants. From this category, Carboxymethyl-cellulose (CMC) has been widely utilized for the depression of talc and siliceous gang minerals, improving the recoveries and grades of copper in the concentrate. The action of CMC as depressant in sulphide flotation is highly dependent on pH conditions. (Bulatovic, 2007)

3.2.5 Eh/pH regulators

The utilization of pulp potential measurements (Eh) and pH as means to control the flotation process for specific minerals has become a popular subject of study. The effect of pH on the electrical potential of the slurry, conductivity, and the oxidation-reduction conditions that drive surface chemistry, their collection and flotation is well documented. (Herrera-Urbina et al., 1999; Götkepe, 2009; Grano, 2010; Woods, 2010)

The Eh/pH conditions are usually recorded and plotted in a diagram that can help to determine what are the stable chemical forms in which a metal ion would result and the chemical species at every combination of the two variables. An example is offered in Figure 4, while Figure 5 presents the effect of pulp potential on the recovery of the most common sulfide minerals.

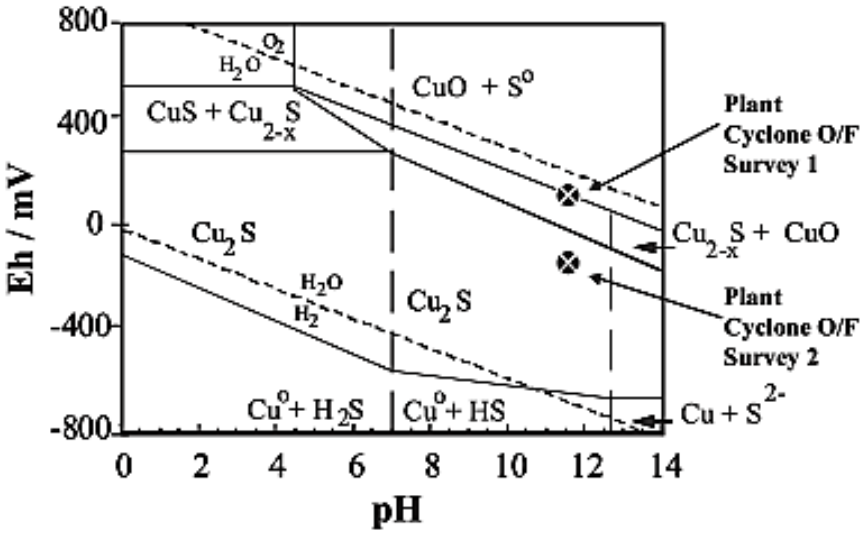

Figure 4. Examples on a cyclone overflow Eh/pH conditions and the stable copper minerals. Survey 1 is with sulphidization, Survey 2 with sulphidization (Grano, 2010).

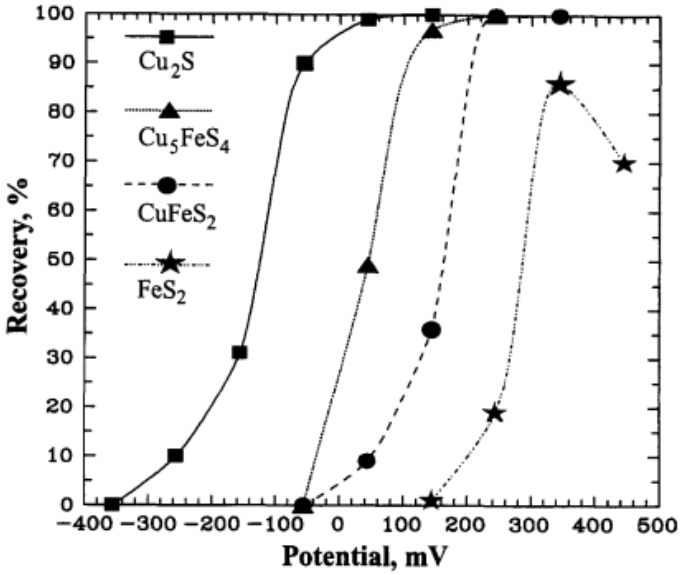

Figure 5. Recovery on flotation circuit of common sulfide minerals as a function of electrical potential (Tolley et al., 1996).

Another potential area of impact for the utilization of Eh measurements in the process, as outlined by Napier-Munn and Wills (2007), is in the field of collector-less flotation, in which by the adjustment of electrochemical properties on the surface of minerals, and at the right particle size, the hydrophobicity of the species is enough to generate natural flotation in the presence of air. Collector-less flotation will not be covered in this review.

3.3 Operational components

3.3.1 Mass pull

Mass pull is an operational parameter that measures the bulk mass recovered in the concentrate phase as a fraction of the mass fed into the process (Anon., 2013). Due to the implementation of machine vision, such as Outotec's Froth Sense® cameras for measurement of froth velocities, the mass pull can be adjusted by utilizing inputs of froth velocity and froth level. The utilization of mass pull in advanced control strategy strives for optimal feeding rates of ore into the flotation bank, as well airflow into the cells and mechanical parameters such as rotor speed for obtaining stable throughput and maximum effect on recovery (Maldonado et al.,

2012). Additionally, mass pull control can serve as a mean to optimize and de-bottleneck the amount of rough concentrate that has to report to the regrinding mill for further liberation and upgrading of product grade, as suggested by Supomo et al. (2008).

3.3.2 Conditioning time

Most of flotation reagents are applied in small dosages and high dilutions into the mineral slurry. Therefore, applying the right conditioning time and dosing points in the flotation circuit are important requirements to achieve the right degree of reagent absorption by the minerals in the slurry as well as promoting the reactions at the particle surface level (Day, 2002). Flotation performance optimization by consideration of conditioning time for different complex sulphide ores has been previously studied utilizing statistical methods by Yuan et al. (1996), Kuopanportti et al. (2000) and Rath et al. (2013),.

3.3.3 Geometallurgy

Geometallurgical information of the mineable ore blocks containing a base level of properties such as mineralogy, hardness and predictions of recovery and product grade are essential inputs on the production planning and plant parameter adjustments for achieving production goals and forecasts. Another important output of correct geometallurgical profiling is the ability to optimize reagent addition based on a series of possible mixture designs. (Bahri et al., 2011)

It has been previously mentioned that the mineralogy of the ore body is critical to the most important performance metrics in a flotation plant. Dean (2010) explains that, in order to be able to make a sensible production planning and plant tuning in terms of ore properties, at least a base level of metallurgical data into the block model of the body should include:

- Assays for determining metal grades. An essential measurement in order to correctly determine the process performance as well as to plan the production accordingly
- Lithology. Including all physical aspects that can be used to characterize ore samples such as color, granule size, texture, small scale structures and mineralization
- Specific Gravity. Important for several unit operations of the concentrator, especially since differences in specific gravity can be used for physical separation in flotation and thickening and have to be considered for feed mixtures
- Magnetic and radiometric properties. Magnetic materials in the ore can be indicative of high iron presence. Additionally, magnetic separation of minerals uses this property for grade improvements or concentration of magnetic vs. non/magnetic minerals
- Mineralization of both ore and gangue minerals. Determining and tracking the mineralization of distinct ore blocks from the pit allows understanding the future needs for the process in terms of variable adjustments that create the best operating profile for a particular mixture. Optimization can be done with strong focus on mineral mixtures
- Hardness (Bond Work Index and Drop Weight Index). One of the most utilized parameters for determining the design and operation of comminution stages for optimal particle size distribution of the ore
- Recovery and concentrate predictions based on mineralogy. After the right parameters have been determined by profiling ore blocks, the optimal set/points can be bound to the mineral mixtures and performance estimates as well as production planning can be based on this information.

3.3.4 Particle size

The probability of a mineral colliding and being collected by an air bubble is largely dependent upon particle size. This means that even at identical mineralogy, if two largely different particle sizes are achieved for minerals, there is high potential for

variation in the flotation kinetics. At the same time, due to differences on grindability and degrees of liberation of the minerals forming an ore, the grades of copper, and therefore the recovery from the various sizes in the feed will exhibit a distribution such as the one displayed in Figure 6.

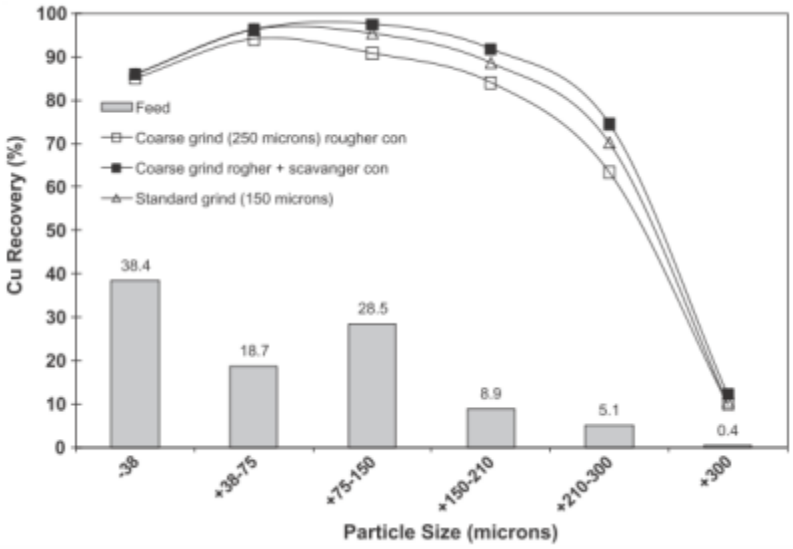

Figure 6. Distribution of copper in the different particle sizes of the feed (bars) and maximum recoveries as a function of these sizes (Farrokhpay et al., 2011).

Particle size has an important effect on reagent consumption, particularly the collector dosage, since the contact angle between bubble and particle is largely dependent on the sizes of both bodies, resulting on an optimal particle size for flotation. (Bulatovic, 2007)

It is important to achieve a correct size distribution after grinding. Some studies (Biswas, 1994; Day, 2002; Bulatovic, 2007; Napier-Munn and Wills, 2011) have determined that if too finely ground, the ore becomes prone to sliming, resulting in excessive coating of both bubbles and copper minerals by the slimes and impeding the proper attachment of the mineral particles to the surface of the bubble. If ground too coarse, the surface does not contain enough liberated mineral and the speed of flotation decreases keeping the particle below the froth bed. The typical cumulative size used in rougher flotation averages 80% of the material under a screen size of 150 μm.

To improve the concentrate quality, the addition of a regrinding stage between the rougher-scavenger and the cleaning stages is usually added, which generates a finer particle size once the slimes have been removed from the concentrate.

3.4 Equipment components

3.4.1 Cell design

The conventional flotation operation is usually carried out in flotation tank cells. A conventional tank cell can have a capacity up to 500 m^3. The slurry is fed to the cell from a feed box situated at the bottom, while being continuously mixed and contacted with the air exiting the mixer shaft in the form of air bubbles. The floatable particles and the air bubbles travel upwards to the froth phase from where they overflow to the launder collection zone to be separated while the hydrophilic gangue minerals travel down within the cell towards the tailings collection zone and exit the cell. (Outotec, 2014)

An alternative to tank cells industrially available since the 1960s are flotation columns. The change in geometrical design, as well as the modification of the feeding points both for the slurry and air inlets confers unique properties for increased contact volume between particles and bubbles. The slurry enters the column approximately at the midpoint, below the froth bed while the air is evenly distributed at the bottom as shown in Figure 7. This allows for a larger contact time, reduced need for mixing and overall increase in the flotation rate (Kawatra and Eisele, 1987). The equipment selection will largely depend on the processing throughput requirements as well as the presence of fines in the slurry.

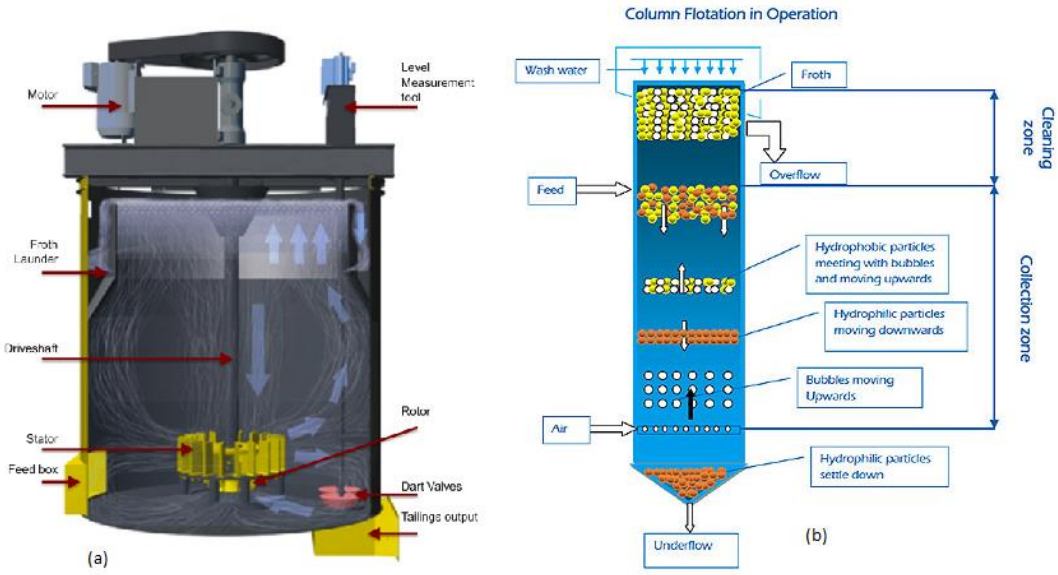

Figure 7. (a) Outotec TankCell® (b) flotation column (Outotec Oy, 2014; Mcnally Sayaji, 2014).

3.4.2 Turbulence and mixing

The proper degree of mixing within the cell is another process variable utilized for flotation control. The rotator speed has to be large enough to create the necessary turbulence for particle and bubble interaction and collision and at the same time not surpass a limit that would disrupt and impede a stable attachment of the minerals. Rodrigues et al. (2001) determined a relationship between particle size, recovery and turbulence that indicates that increases in particle size result in a linear increase in collision before falling recovery results beyond threshold turbulence as exemplified in Figure 8 by the study of recovery of glass beads and quartz particles at various turbulent regimes.

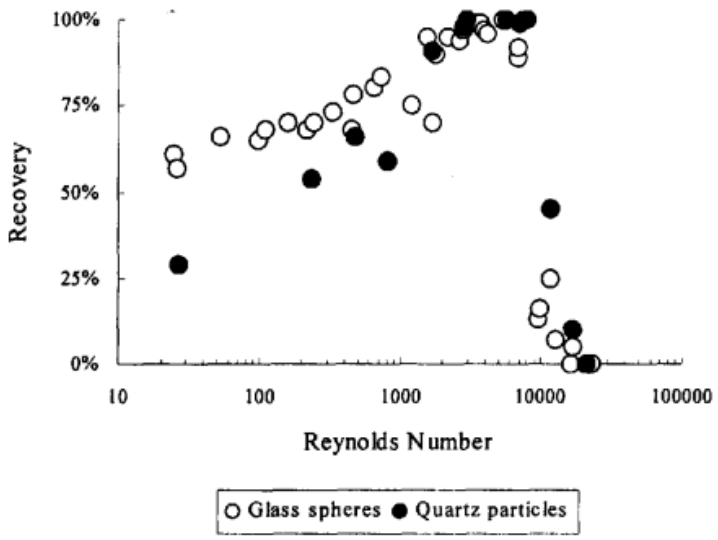

Figure 8. Microflotation response of glass spheres (class B) and quartz particles (0.208-0.295mm) versus impeller Reynolds number. (Rodrigues et al, 2001).

3.4.3 Air flow

A basic relationship between air flow and flotation performance can be explained by the effect of increasing the volume of air into the cell, which results in more bubbles available for collection and decreased residence time of the bubbles traveling upwards. Therefore, a right balance will be established between the correct level of aeration, selectivity and recovery. (Drzymała, 2007)

3.4.4 Process configuration

Due to the changing conditions in the ore mineralogy, sometimes small adjustments in the process configuration, or, better put, redirection of streams can result in improved results as compared to the generic array for the operational base case. In this regard, Malghan (1986) proposed three major strategies for process optimization related to the flotation banks configuration:

- Screening and bypassing the finest particles from the rougher concentrate could result in reduction of regrinding energy and increasing the regrinding capacity prior to cleaning

- Bypassing the first 2 minutes rougher concentrate after a startup of the process could prevent copper losses due to over grinding the already liberated copper particles and hence rendering them difficult to recover
- Monitoring water pH from recycled tailings dam and redirecting it to process areas where pH sensitivity is less critical to performance.

4 Theoretical models for flotation

The flotation of particles in each individual cell or circuit is a time dependent process that can be modeled with the aim of designing different circuit configurations or selecting values for the operating parameters, such as the ones reviewed in the previous chapter sections. Using batch flotation laboratory tests, it is possible to determine either a first order dynamic model with an approximate flotation rate constant, or regression models obtained from statistically reliable data that consider select variables of relevance to the problem of study. Traditionally, the most widely utilized theoretical model for prediction of recovery is presented by Gorain et al. (2000) in equation 3:

$$\frac{dW}{dt} = -kW \qquad (1)$$

Where W represents the mass of mineral particles to be floated at time t and k is the overall flotation rate constant.

4.1.1 Flotation rate constant

The flotation rate constant (*k*) can be determined from a simple batch flotation cell by collecting the recovery results in respect to time and determining the tangent line to the curve as shown in Figure 9. One of the major drawbacks of utilizing such first order dynamic models is that the results are exclusive to the conditions of the test and the scalability of results has to be modified by safety factors ranging from 100% to 300% for circuit design (Gorain et al., 2000). The flotation rate constant

becomes then a highly hypothesized parameter that cannot account for changes in the mineralogy of the ore, particle size distribution, operating conditions or equipment characteristics such as geometrical design.

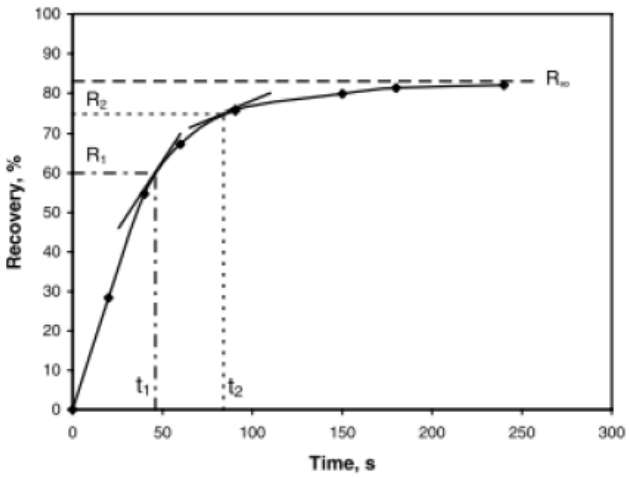

Figure 9. An example of a recovery vs. time curve from a batch flotation test and the tangent lines representing the change in flotation rate as the floatable particles leave the slurry phase (Gupta and Yan 2007).

In practice, a different flotation kinetic curve has to be developed in order to profile the different responses of the numerous circuit configurations, reagent matrices and feedstock qualities to generate response predictions.

5 Response Surface Methodology (RSM)

Response Surface Methodology (RSM) is a compilation of mathematical and statistical methods, with roots on the chemical and process industries dating back to 1951 by the works of Box and Wilson that explores the effects of multiple variables on one or more responses of a noisy and often difficult to model system.

Through the collection of results from a series of controlled experimental designs and the application of linear regressions, it is possible to study engineering systems within the limits set by the levels of the studied variables. The data collected from the experiments as results can be used to obtain statistical models that can be

optimized for one or more responses of the system (Del Castillo, 2007; Myers and Anderson-Cook, 2009). Figure 10 presents the approach to a flotation system seen as a black box and the variables intended for study.

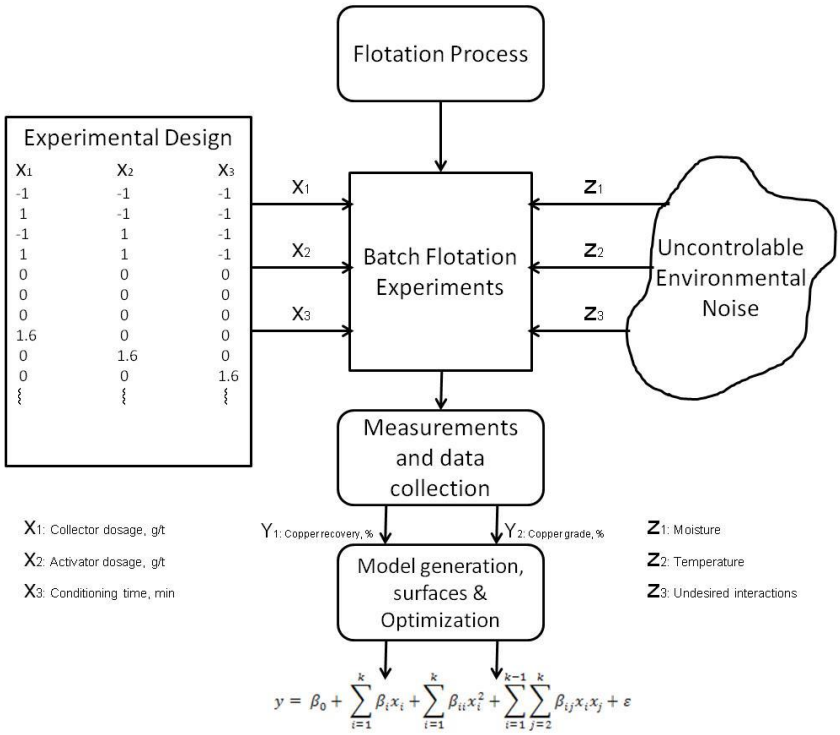

Figure 10. Flotation process as a black box with its predicting variables, responses and noise components. Adapted from Del Castillo (2007).

The Response Surface Methodology consists of the following steps:

- Perform a series of factorial designs for parameter screening if no process historical data is available for variable selection
- If plant data is available, perform a Pareto analysis to determine the variables (predictors) that have the greatest influence on the process responses that are to be modeled and the middle value for them as the starting point or base case for the experiments
- Select the resolution of the model and design a series of experiments that include well defined levels (lower, middle and upper) of the influencing variables while keeping all other experimental parameters as constant as possible

- Collect the results for every response and through an Analysis of Variance (ANOVA) procedure, determine which second order effects and interactions between the variables are statistically significant for the model at the established confidence level. After this, select the model coefficients and generate the model for the response and its surface plot
- Define the optimization goals for minimizing or maximizing the responses and perform the optimization of the model via overlaying the response plots or with a stochastic approach

When using measurable variables and responses, the response surface model can be expressed in the following manner:

$$\boldsymbol{y = f(x_1, x_2, x_3, \dots, x_k)} \quad (2)$$

Where *y* represents a response of the system and x_k represents the measurable independent variables called factors. As a second order model, it is possible to appreciate the interaction effects of the variables as represented in equation 5:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

Where β represents the unknown parameters for main, combined and higher order effects of parameters on the system, estimated by the least squares regression and ε represents the random error built into the model and assumed to present normal distribution with mean value of zero and a variance that is uncorrelated to the model parameters. From this basic model, it is possible to derive linear, quadratic and two factor interaction models that describe the system accordingly.

5.1 Mixture and central composite designs

The changing nature in terms of mineralogy for a porphyry ore body demands for the creation of different feed blends for attaining desirable production goals. A

mixture design is a special kind of response surface experiment in which its components have fractional levels of an unit representing the total composition of the feed, as opposed to experiments designed solely based on operational parameters in which the levels of such variables are independent from the other variables that create a cuboidal or spherical experimental region (Myers and Anderson-Cook, 2009). A special type of designed experiments for mixture and process variables can handle both types of variables in the same design by transforming the fractional values of the mixture composition to the coded variables in which process parameters are handled (low, medium, high and axial design points). Figure 11 presents a schematic representation of mixture and cuboidal designs.

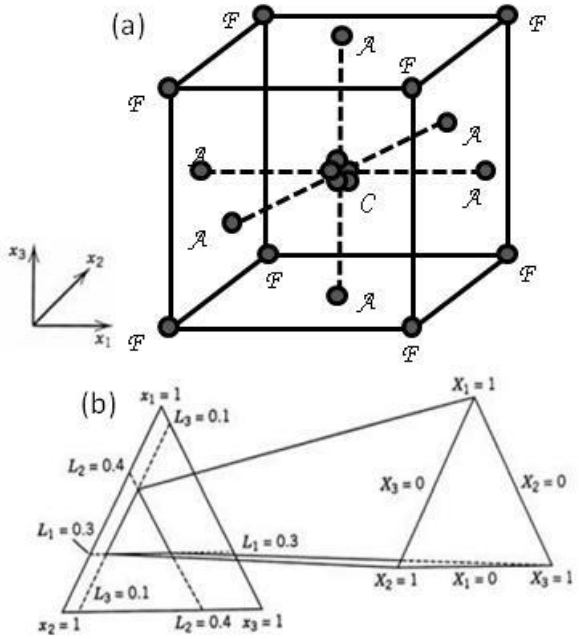

Figure 11. (a) Central Composite Design (CCD) for process variables. (b) Constrained mixture design (Oehlert, 2000; Myers and Anderson-Cook, 2009).

In the example above, the factorial points (F) represent the coded values of the three process variables used in the design (1, -1) for low, and high. The axial points (A) are added to the design in order to augment the experimental region and generate a rotatable orthogonal design fit for a second order model (-1-α, 1+α), while the center points (0, 0, 0) are used to avoid lack of fit in the model as well as to provide a better estimation of the error (Del Castillo, 2007). On the other hand,

the pyramid in Figure 11 represents a constrained mixture design, in which the mixture is never composed of a pure component, but rather specified with upper and lower values.

By combining both designs, it is possible to create an experimental region in which the different levels for a mixture design can be tested for different treatments of process variables, allowing to create an empirical model that can be utilized for process optimization and the creation of an optimal feed composition for a process such as flotation, as displayed in Figure 12. The empirical model for a 3 component mixture becomes:

$$y = \sum_{i=1}^{3} \beta_i x_i + \sum_{i<j}^{2} \sum_{j=2}^{3} \beta_{ij} x_i x_j + \sum_{k=1}^{2} \left[\sum_{i=1}^{3} \alpha_{ik} x_i + \sum_{i<j} \sum_{j=2}^{3} \alpha_{ijk} x_i x_j \right] z_k + \left[\sum_{i=1}^{k} \delta_{i12} x_i + \sum_{i<j} \sum_{j=2}^{k} \delta_{ij12} x_i x_j \right] z_1 z_2 \quad (4)$$

In this model the mixture components are represented by x_{ij} and the effect of the individual components, as well as the effects of the interactions between the components is present in the first two items in it. Next, the effect of the process variables represented by z_k both individually and in combined effect is calculated for every mixture combination. While being an extensive model that can be expanded to different order equations, it is possible to reduce it by testing hypotheses on individual model parameters and leaving only the parameters that bring any significance to it. (Anderson-Cook, 2009)

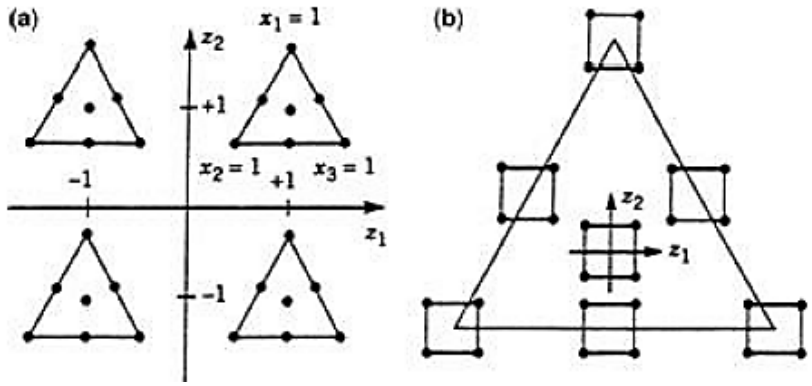

Figure 12. Combined design for mixture components and process variables (Anderson-Cook, 2009).

5.2 Applications of Response Surface Methodology in minerals processing industry

Originally developed from chemical processing research by Box and Wilson (1951), RSM has found numerous applications in the minerals processing industry, where it has been utilized for a variety of process optimization studies.

5.2.1 Chromite concentration

On the chromite concentration process by multi-gravity separators, Aslan (2008) performed a multi-objective optimization targeting operating variables such as drum speed, tilt angle of the drum, wash water flow-rate and shake amplitude; obtaining results that increased concentrate grade and recovery from approximately 42% and 65% to 48% and 74% respectively.

5.2.2 Leaching of ores

RSM has also been applied in hydrometallurgy, particularly in the application of leaching processes for metal recovery. Massacci et al. (1998) studied the influence of operating conditions of temperature, oxidant concentration and particle size of the mineral in the leaching of a complex sulphide ore. Through the study of the interaction effects of the variables, such as temperature and oxidant concentration, they found negative effects in zinc recovery as the ratio between increases between

the first two increased, which resulted in the need to offset this effect by better liberation, and hence a reduction of particle size. Çoruh et al. (2012) carried out an optimization study on a copper leaching process from flotation waste for environmental remediation. They created a surface model for establishing the optimal pH conditions, stirring time and temperature. The results, however, indicated the need for finding the curvature point in the system for further development.

5.2.3 Electrocoagulation

Behbahani et al. (2011) worked on the removal of fluoride by the use of an electrocoagulation process. The study considered the initial concentration of fluoride in the feed material, along with pH conditions, current density and reaction time as the main predictors for modeling the removal efficiency with a high degree of reproducibility.

5.2.4 Ore mixture designs

Van Tonder et al. (2010) utilized mixture designs to study the antagonistic and synergetic effects that ore blends of different mineralogy displayed in terms of grinding performance and floatability of particles in a platinum concentrator. The model was then optimized to determine the right fractions of each ore from different sites for optimal recovery of platinum. Bahri et al. (2011) also created mixture designs for characterization and optimization of recovery and ash content in a coal washing circuit for coal feed material proceeding from different sources.

Several studies have been performed on the flotation process that includes the use of RSM, being the minerals processing field where most of the applications of this methodology are currently found.

5.2.5 Froth flotation

Martinez et al. (2003) applied the methodology to a celestite flotation process by evaluating the celestite grade variations in the feed, pH conditions and dodecyl sulfonate as collector. Aslan and Fidan (2008) carried out a study for a lead flotation process in which a similar collector (PAX) dosage, Sodium Sulfide (Na_2S) as activator and pH were used as predictors for predicting recovery and grade of product. Mehrabani et al. (2010) modeled and optimized a flotation process of sphalerite using a Central Composite Design (CCD) for the recovery of zinc and lead. Four models were generated for multiple responses such as recoveries for both metals and extraction efficiencies. Their study focused on collector (PAX) dosage, activator ($CuSO_4$) concentration and pH as the major variables. Rath et al. (2013) utilized a Pareto analysis to determine that pH, collector and dispersant concentration, and conditioning time were the most critical variables for the treatment of hematite by flotation for the recovery of iron. The study served to model equations for recovery and grade of the concentrate and to determine the importance of conditioning time.

More studies include the work performed by Dehghani et al. (2012) for the optimization of phosphate and iron recovery studying pH, solids content of the feed, conditioning time and reagents. The work by Aslan et al. (2008) simultaneously optimized kerosene and depressant dosage, scrubber agitation speed and scrubbing time for graphite production. Naik et al. (2005) optimized the reagent dosages and interaction effects between them in the flotation of fine coal particles. On the copper flotation process, Nanthakumar and Kelebek (2007) detailed the interactions between ethylenediamine tetraaceticacid (EDTA) and triethylenetetramine (TETA) as surface activators and PAX as collector on a stage-wise optimization of a flotation process of oxidized pentlandite and pyrrhotite as main mixture components. On a similar way, Vazifeh et al. (2010) used surface modeling by a factorial design on collectors and frother dosages for reagent screening and selection, later obtaining response models for recovery and concentrate grade.

In summary, RSM has demonstrated a large potential for implementation in the tailored modeling of processes, fine tuning of parameters and the possibility for utilizing the optimized models for a series of production planning activities, supply chain and forecasting of production goals based on the results from the studies. Moreover, the wide range of studies focusing on, e.g., different reagents of the same families clearly show the potential for exploring the application also for flotation process design.

EXPERIMENTAL WORK

In the experimental part of this thesis, ore samples from an Outotec's customer were tested at Outotec's Research Center in Pori, Finland.

The tests were limited to the rougher stages of the flotation process and did not consider multiple concentrate collection for the determination of flotation rate constant. For the purpose of modeling and optimization, only the final responses in terms of recoveries of the different elements and grades in the product were needed. Furthermore, previous studies of the ore determined that the optimal flotation time in the rougher stage for copper was 13 minutes, which was the basis for the study.

6 Aim of the Study

This thesis has the objective of evaluating the viability of utilizing the Response Surface Methodology for customer cases from the Operation and Maintenance organization. Due to the nature of the services offered by such organization, the methodology would be utilized for the optimization of process performance by the execution of studies anchored in varying responses and processing strategies to attend the customer needs and requirements to Outotec. In addition, the broad range of technologies offered by Outotec for its customers, such as online grade and particle size analyzers, among other advanced control equipment, can serve as an important source of data for RSM studies.

Another important area of implementation would be as an aid to remote monitoring services offered by Outotec, in which RSM could help determine alternative set-point values while remote monitoring systems would help to keep track of the resulting changes.

The present study serves as a case examination of a copper-zinc flotation process where it was determined that the variables to be manipulated in batch flotation tests would be collector and depressant dosages, as well as pH conditions in the rougher stage of copper flotation.

A satisfactory solution (treatment) would be one that would meet the quality specifications in terms of grades of the desired and penalty components of the concentrate, while maximizing recovery of copper at the lowest possible additions of collector, depressant and lime for pH adjustment.

The study was conducted in two stages. In the first stage of the experimentation process, the responses to different treatments were collected, modeled and optimized. The second part consisted of confirmation tests that validate or disprove the accuracy of the predicted optimal treatment by replicating three times the test under such determined optimal conditions at the set level of confidence.

7 Materials and methods

7.1 Materials

7.1.1 Ore

A sample of approximately 150 kg of ore was collected after the crusher at the site prior to the grinding stage. Only a fraction of this sample was designated for this study (approximately 38 kg).

Data from previous studies on the same operation, as well as historical data from site determined that the flotation feed size to be utilized would be P_{80}=75 µm. The natural pH of the samples measured after grinding and prior to flotation was on average 9.2 for every sample. Table 2 presents the ore elemental grades on average for all samples.

Table 2. Metal content composition of the studied samples.

Copper, %	Nickel, %	Iron, %	Magnesium, %	Sulfur, %
0.47	0.29	10.0	13.2	1.8

7.1.2 Water

The flotation experiments were carried out using fresh tap water from Pori, Finland. Although water quality could have some impact in the study results, mainly due to differences in water pH and concentrations of ions elements such as Ca^{+}, these effects were deemed as negligible for the purpose of modeling the overall behavior of the rougher flotation system.

7.1.3 Reagents

The reagent selection for the study was set from the beginning and in accordance with the reagent matrix currently utilized at the plant, which had been previously screened for process design purposes and different studies performed at Outotec Research Center. Since rougher flotation for copper is the scope of this thesis, the most important reagents for this stage are collector, frother and lime for pH adjustment. In addition, the benefit from adding depressant at an early stage of the process in order to depress siliceous gangue minerals was considered worthwhile of study, hence the decision to include CMC in the rougher flotation reagent matrix.

7.1.3.1 Collector

The choice for collector was a phosphine based collector with high performance in copper-zinc ores. This collector has a high selectivity against iron sulfides such as pyrite and pyrrhotite. As some Cytec (2010) case studies show, in most cases, it naturally requires lower dosages compared to xanthate collectors for certain mineralogies. Figure 13 shows the collector formula.

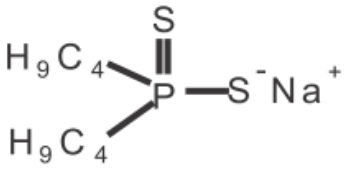

Figure 13. Phosphine based collector.

This reagent was diluted to a liquid solution at 1% concentration prior to its addition.

7.1.3.2 Frother

The choice for frothing reagent was one based on ethylene glycol monobutyl ether, same as the one used in the client's plant. The molecular structure is pictured in Figure 14.

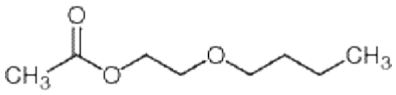

Figure 14. Molecular structure of ethylene glycol monobutil ether.

7.1.3.3 Lime as pH regulator

Calcium hydroxide ($Ca(OH)_2$) is added as a pH regulator. The maximum attainable pH by lime addition is close to 12.5. When lime is added to the slurry, it dissociates in Ca^{2+} and OH^- ions. While the OH^- ions have the direct effect on pH, the presence of Ca^{2+} has important superficial effects on pyrite and pyrrhotite, which, above pH 11 become naturally depressed (Napier-Munn and Wills, 2011). The dosage of lime was performed while closely monitoring the pH electrode with consistent results.

7.1.3.4 Carboxymethyl-cellulose as depressant

Carboxymethyl-cellulose (CMC) is an anionic polymeric depressant widely used in sulfide flotation against hydrophobic gangue minerals such as talc ($Mg_3Si_4O_{10}(OH)_2$). Its efficiency is directly bound to the electric potential and pH of the slurry (Bulatovic, 2007). It was prepared to a 1% concentration aqueous solution prior to its addition in the conditioning phase.

7.1.4 Ball mill

A laboratory-scale ball mill was used in order to attain the particle size of P_{80}= 75 µm. The mill was loaded with a batch of stainless steel balls containing 3.3 kg of 27 mm and 8.7 kg of 19 mm diameter balls as shown in Figure 15. The slurry was composed of a total of 1.5 kg of ore and 0.8 l of water for every batch.

Figure 15. Open and closed ball mill with ball load and ground slurry.

7.1.5 Flotation machine

Outotec-GTK LabCell™ was utilized for these experiments. One of the main advantages of using this machine was the presence of automatic scrapers that remove the froth from the cell at predefined and constant cycles, reducing the error from a manual removal. A squared cell of 4 liters capacity was used in the experiments, along with a number of trays for froth and tails collection. Water and air addition were conducted through the main rotator shaft and alternatively water could be added with a peristaltic pump from an external source to perform fine adjustments of slurry level as the mass is removed from the cell. Additionally, the peristaltic pump was used in reverse mode for the removal of tailing samples for assays while keeping good mixture of the slurry before ending of each experiment. Figure 16 displays the flotation machine with its components.

Figure 16. Outotec-GTK LabCell™ flotation machine and an example of the first froth formed in one of the experiments.

7.1.6 Filters and drying lamps

Positive pressure and vacuum filters were utilized to perform the dewatering operations of concentrates and tails. Depending on the amount of material to be dewatered, the positive pressure filters were used for large amounts while the negative pressure ceramic filters were used for small amounts.

7.2 Experimental design and procedure

This section will be divided in the experimental design and experimental procedure utilized. There is an emphasis in the experimental design, since a large part of a successful RSM study relies on the selected variables to be changed through the experiments, as well as the limits that represent the operating limits for the continuous range of values for such variables. Moreover, the importance of randomization, blocking, and presentation of the experimental matrix is presented on the design part, while the procedure will cover the steps followed to perform the experiments in a standardized way.

7.2.1 Experimental design

The experimental design was assisted by the use of Design Expert software, currently in its 9th version, for selection of methodology, design of the experimental matrix including randomization and blocking, as well as modeling, statistical analysis and optimization of the responses.

Figure 17, and subsequently Table 3 show the experimental space for both factorial and axial points. It is worth noting that only factorial points represent the prediction space used for optimization, while both factorial and axial points are used to gather data about the system and the responses to obtain the model.

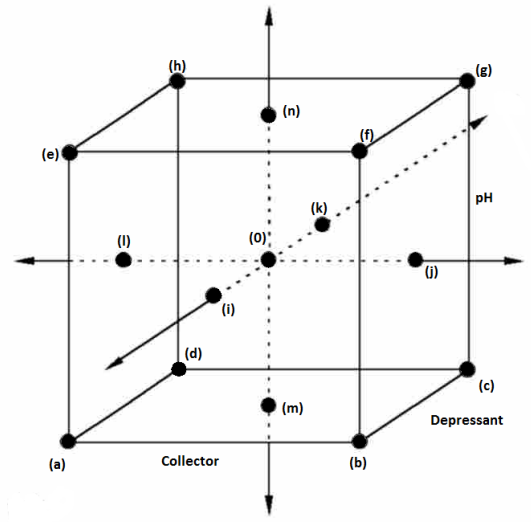

Figure 17. Central Composite Design (CCD) for the rougher flotation system and the selected process factors.

Table 3. Randomized CCD experimental design with center points and variable values for the factors.

Run order	Label in cube	Type	Collector dosage g/t	Depressant dosage g/t	pH
1	(c)	Factorial	42.9	80.7	9.9
2	(f)	Factorial	42.9	24.3	11.8
3	(0)	Center	32.5	52.5	10.9
4	(0)	Center	32.5	52.5	10.9
5	(h)	Factorial	22.1	80.7	11.8
6	(a)	Factorial	22.1	24.3	9.9
7	(0)	Center	32.5	52.5	10.9
8	(e)	Factorial	22.1	24.3	11.8
9	(g)	Factorial	42.9	80.7	11.8
10	(d)	Factorial	22.1	80.7	9.9
11	(0)	Center	32.5	52.5	10.9
12	(b)	Factorial	42.9	24.3	9.9
13	(n)	Axial	32.5	52.5	12.5
14	(m)	Axial	32.5	52.5	9.2
15	(k)	Axial	32.5	100.0	10.9
16	(0)	Center	32.5	52.5	10.9
17	(i)	Axial	32.5	5.0	10.9
18	(0)	Center	32.5	52.5	10.9
19	(l)	Axial	15.0	52.5	10.9
20	(j)	Axial	50.0	52.5	10.9

A total of four responses were selected in order of importance. They all relate to the rougher concentrate composition and are presented as follows:

- Copper recovery %: The main response to be maximized. Copper represents the main product at this stage of the process. The collector is specific for copper sulfide minerals primarily, as well as nickel sulfide minerals.
- Copper grade %: This response was tracked in order to assess the enrichment ratio from the first stage of the copper concentration by flotation. While no values or ranges are set for optimization, it was considered worth keeping the information for the concentrate grade to assess model behavior against theoretical knowledge and prediction purposes.
- Iron recovery %: Since iron is not a target element in either copper or nickel concentrates, the aim at this stage is to minimize the amount of iron minerals present in the rougher concentrate in order to ease the cleaning

stage for copper, as well as to have a higher copper grade in the copper concentrate. Lower iron also means lower challenges in the smelting and converting phase at the refinery.

- Nickel recovery %: As mentioned earlier in this thesis, nickel concentrate is a second product from the concentrator. Ideally, a small amount of nickel would be carried in the copper concentrate. In practice, however, pentlandite behaves similarly to chalcopyrite to the specific collector utilized; the main driver in the difference in magnitude of the responses of these minerals would be pH.

7.2.2 Experimental procedure

The experimental procedure consisted of ore grinding, batch flotation, concentrate and tails filtration and chemical assays for metal content estimation. This section will describe the steps in detail as it was performed for all twenty initial experiments and subsequent three confirmation tests. Figure 18 represents the simplified diagram for the experimental steps.

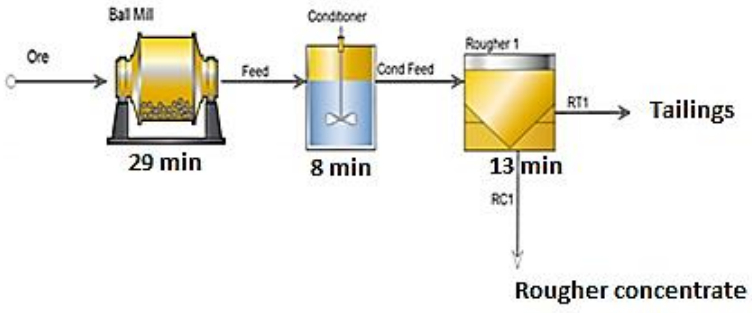

Figure 18. Simplified diagram for flotation experiments.

7.2.2.1 Size reduction (crushing and grinding)

The samples were first crushed in a laboratory scale jaw crusher to a size of 100% passing a 1.18 mm sieve. After this, the bulk of the ore was separated into individual samples with a vibratory feeder to a rotary tube divider, ensuring no sample segregation or non-homogeneous mixture would be avoided. All samples

consisted in 23 bags of 1500 grams each. Using an optimal grinding time of 29 minutes, every sample was ground to a P_{80}=75 µm in the laboratory scale ball mill. Slurry containing approximately 65% solids was prepared by adding 0.8 liters of water to the ore prior to grinding. The ground slurry was then transferred onto a bucket for transportation and immediately after to a flotation cell of 4 liters capacity. Figure 19 presents the approximate particle size distribution of the samples after grinding

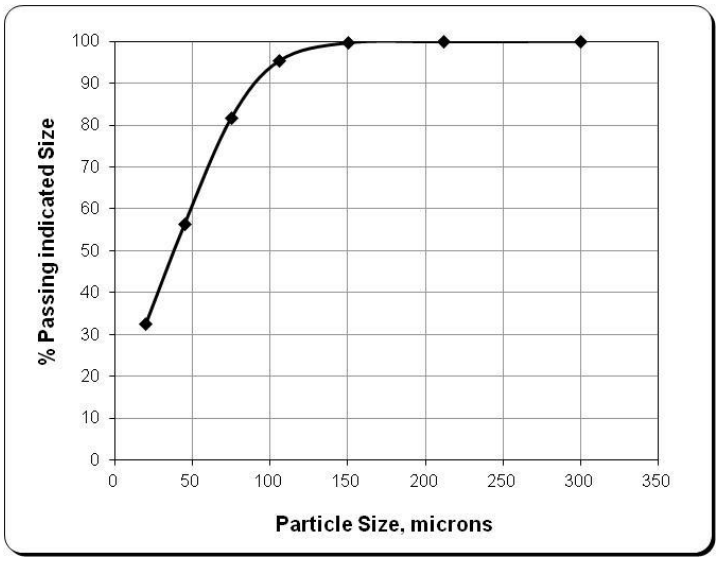

Figure 19. Particle size distribution for the ground ore.

7.2.2.2 Conditioning

After preparing the reagents to their respective 1% dilutions, an adjustment between the indicated grams per ton dosages to liquid volumes had to be calculated. Table 4 presents the volumetric equivalents to the selected dosages, as well as the conditioning time applied before beginning of flotation. The order of conditioning was first the depressant (CMC), followed by collector, frother and lastly lime for pH adjustment. The conditioning was performed always in the flotation cell without air addition and aided by the rotor of the flotation machine.

In practice, reagents are not usually added in diluted form at plant scale. This is necessary in laboratories due to the smaller volumes and ore samples in order to have better control and precision over the dosing of the reagents.

Table 4. Adjusted dosages from g/t to ml of aqueous solution.

Depressant (CMC) 5 minutes		Collector 2 minutes		Frother 1 minute
5 g/t	0.75 ml	15 g/t	2.25 ml	35 g/t 5.25 ml
24.3 g/t	3.64 ml	22.1 g/t	3.31 ml	
52.5 g/t	7.88 ml	32.5 g/t	4.88 ml	
80.7 g/t	12.11 ml	42.9 g/t	6.44 ml	
100 g/t	15 ml	50 g/t	7.5 ml	

7.2.2.3 Flotation

The flotation stage of the experiments begins after conditioning of reagents and pH adjustments. The tests were performed with a constant rotor speed of 1800 rpm and an airflow rate of 3 l/min. the scraping cycles were set to 4 second intervals and with enough room to not interfere with the pH probe inserted at the edge of the cell.

After conditioning, the air valve was opened and a period of 30 seconds for air mixing is held. After those initial 30 seconds, the scrappers were initiated and the froth was collected in a tray set under the overflowing cell. The cell, rotor and scrapers were constantly sprayed with a mist of water to avoid over-accumulation of rich froth in the edges surrounding these structures. A water level mark was drawn to target and maintain constant slurry level in order to compensate for the liquid losses through the leaving froth. Water was added through an external hose and by a peristaltic pump that is fed from an external water container.

The scrapping cycle was stopped immediately after the 13 minutes of flotation, followed by the closing of the air valve. The rotor was kept on in order to maintain homogeneous mixing and to collect a representative sample of approximately 200 ml of tailing slurry to be analyzed. After this was completed, the rotor and flotation machine were stopped for final tails collection. All concentrate and tails samples were properly labeled and the machine and flotation cell had to be properly cleaned to avoid contamination in the following tests.

7.2.2.4 Filtration and drying

After concentrate and tails samples were collected following flotation of the mineral, they were dewatered and dried utilizing positive pressure cylindrical filters for bulk tails and negative pressure ceramic filters for concentrate and analyze sample (tails).

Prior to filtering, a total of three square shaped brown papers per test had to be cut to approximately 50 cm per side and folded twice to hold the filtering media and the filtered sample in place. The brown squares and filter media were carefully weighted and labeled with the combined mass and sample to properly record the dry mass of the samples after drying in the lamps at the laboratory.

After the samples were dried in a period of approximately 12 hours, they had to be weighted, the final mass recorded, followed by pulverization and packaging for the final elemental assay in the laboratory by ICP (Inductively Coupled Plasma) technique for metals and LECO carbon and sulphur determinator for sulphur. In accordance to the elemental assays of the feedstock material, the assays for concentrate and tails covered Cu, Fe, Ni, Mg, and S.

8 Analysis of results and discussion

This section will present the results attained for each of the four responses defined for the system. It will also cover the main metallurgical calculations for recovery and other important parameters such as concentration and enrichment ratio. After presenting the final calculated data, a detailed explanation of the analytical work is presented. It is considered important to involve the reader in the multiple considerations and steps necessary to perform the regression, select the right and most suitable model for every response, understand the main features of every model through an analysis of variance (ANOVA), as well as the process of model reduction or expansion in order to fit it better to the data and for it to become useful for predictions and optimization.

Another important aspect to mention is that, due to the axial points in the design, the highest values in pH generated higher error in the responses, therefore, an explanation of the standard error and safe intervals will be presented.

8.1 Experimental results and calculations for response data

Table 5 represents an expansion of Table 3 with the elemental contents in concentrate and tails for copper, nickel and iron.

Table 5. Multi-elemental grades in concentrate and tails for each experiment from samples elemental analysis.

Run order	Type	Collector dosage g/t	Depressant dosage g/t	pH	Cu grade %		Ni grade %		Fe grade %	
					Conc.	Tail	Conc.	Tail	Conc.	Tail
1	Factorial	42.9	80.7	9.9	8.3	0.07	3.5	0.13	20.6	9.6
2	Factorial	42.9	24.3	11.8	9.8	0.11	0.7	0.27	17.2	9.9
3	Center	32.5	52.5	10.9	9.2	0.08	1.8	0.22	19.3	10.0
4	Center	32.5	52.5	10.9	8.7	0.08	1.8	0.21	18.9	9.7
5	Factorial	22.1	80.7	11.8	11.3	0.12	0.7	0.27	18.3	9.7
6	Factorial	22.1	24.3	9.9	8.8	0.08	2.8	0.17	19.5	9.5
7	Center	32.5	52.5	10.9	8.6	0.08	1.8	0.22	18	9.6
8	Factorial	22.1	24.3	11.8	9.9	0.14	0.6	0.27	16.7	9.7
9	Factorial	42.9	80.7	11.8	9.1	0.11	0.7	0.27	16.7	9.7
10	Factorial	22.1	80.7	9.9	10.7	0.10	2.6	0.20	20.8	9.6
11	Center	32.5	52.5	10.9	7.8	0.08	1.8	0.20	17.7	9.7
12	Factorial	42.9	24.3	9.9	7.3	0.08	2.5	0.16	18.1	9.5
13	Axial	32.5	52.5	12.5	6.9	0.24	0.4	0.28	13.9	9.7
14	Axial	32.5	52.5	9.2	7.4	0.08	2.9	0.14	18.7	9.5
15	Axial	32.5	100.0	10.9	8.3	0.08	1.8	0.21	18.4	9.6
16	Center	32.5	52.5	10.9	8.0	0.08	1.6	0.22	17.7	9.6
17	Axial	32.5	5.0	10.9	8.3	0.08	1.4	0.23	17.4	9.5
18	Center	32.5	52.5	10.9	8.8	0.09	1.7	0.22	18.5	9.4
19	Axial	15.0	52.5	10.9	9.7	0.09	1.3	0.24	18.7	9.5
20	Axial	50.0	52.5	10.9	7.5	0.08	2.0	0.19	18.3	9.4

According to Napier Munn and Wills (2007), metal recovery is usually calculated in laboratories and plants by utilizing only the assay results in terms of metal content in feed (*Ff*), concentrate(*Cc*) and tails(*Tt*) as shown next.

From the mass balance for the mineral

$$\boldsymbol{F = C + T} \quad (5)$$

Followed by the copper balance

$$\boldsymbol{Ff = Cc + Tt} \quad (6)$$

The balance is transformed to

$$Ff = Cc + (F - C)t \quad (7)$$

By regrouping factors

$$C(c-t) = F(f-t) \quad (8)$$

Since copper recovery is the percentage of the initial copper in the feed transferred on to the concentrate Cc/Ff

$$\frac{C}{F} = \frac{f-t}{c-t} \quad (9)$$

And

$$\frac{Cc}{Ff} = \frac{c(f-t)}{f(c-t)} \cdot 100\% = \boldsymbol{Cu\ Recovery}\% \quad (10)$$

The term *c/f* represents the enrichment ratio, another important metric that facilitates the evaluation by what factor the copper grade has increased after a single stage of flotation. Example calculations are presented for the first test.

Copper recovery equals:

$$Cu\ Rec\% = \frac{8.3(0.47-0.072)}{0.47(8.3-0.072)} \cdot 100\% = \mathbf{85.4}\% \quad (11)$$

With an enrichment ratio of

$$\frac{c}{f} = \frac{8.3}{0.47} = \mathbf{17.66} \quad (12)$$

Table 6 summarizes the recoveries of the aforementioned elements as well as the copper grade to generate the main data set for the modeling of the system.

Magnesium grades and recoveries were excluded due to a high amount of error in the results and large variance in grades and recoveries. It was still determined that the study was successful since copper and nickel recoveries and grades were in accordance to pre-existing cases from customer's operations and presented acceptable variance. However, for center runs, only copper presented constant results in the first phase, for the rest of the responses, a greater variance was observed in the results.

Table 6. Multi-elemental recoveries, ratio of concentration and enrichment ratio based on copper grades.

Run order	Collector dosage g/t	Depressant dosage g/t	pH	Cu recovery %	Cu grade %	Ni recovery %	Fe recovery %	Copper enrichment ratio
1	42.9	80.7	9.9	85.4	8.3	58.0	7.3	17.6
2	42.9	24.3	11.8	77.3	9.8	9.6	2.1	20.8
3	32.5	52.5	10.9	83.3	9.2	26.1	0.8	19.5
4	32.5	52.5	10.9	83.8	8.7	30.0	5.8	18.4
5	22.1	80.7	11.8	74.9	11.3	12.7	6.2	24.0
6	22.1	24.3	9.9	83.9	8.8	44.7	9.6	18.8
7	32.5	52.5	10.9	84.2	8.6	26.3	8.6	18.3
8	22.1	24.3	11.8	70.8	9.9	9.9	7.8	21.0
9	42.9	80.7	11.8	76.9	9.1	13.4	6.7	19.3
10	22.1	80.7	9.9	79.3	10.7	33.0	7.4	22.8
11	32.5	52.5	10.9	83.4	7.8	33.5	7.3	16.6
12	42.9	24.3	9.9	83.9	7.3	47.8	10.5	15.5
13	32.5	52.5	12.5	50.7	6.9	10.9	9.6	14.8
14	32.5	52.5	9.2	83.9	7.4	54.3	10.0	15.8
15	32.5	100.0	10.9	83.8	8.3	31.2	8.0	17.6
16	32.5	52.5	10.9	83.6	8.0	26.4	9.8	17.0
17	32.5	5.0	10.9	83.2	8.3	23.6	10.4	17.6
18	32.5	52.5	10.9	82.7	8.8	27.0	11.6	18.8
19	15.0	52.5	10.9	81.0	9.7	20.7	11.1	20.5
20	50.0	52.5	10.9	84.7	7.5	36.4	12.3	16.0

8.1.1 Copper recovery, grade and enrichment ratio

8.1.1.1 Copper Recovery %

Copper recoveries ranged between 50.7% and 85.4%. Copper grades in concentrate ranged between 6.94% and 11.3% and enrichment ratio was in the range between 14.8% and 24%.

It is important to note that the lowest values in all copper related figures, excluding the enrichment ratio, were obtained from the 13th run, an axial point that was performed at pH 12.5, which was near the saturation point for lime, as well as being an unfeasible operating point for a rougher concentration for copper. The low performance of this test can be explained due to the exponential increase in lime in order to attain such high pH value. Table 7 presents the equivalent dosages of lime

for the five different pH values. In comparison to the next highest pH of 11.8, the lime dosage represents approximately a five-fold increase, from 1.7 kg/t for the latter to 8.73 kg/ton for the former.

Table 7. Average lime addition and dosages for the designed pH values.

pH value	Average lime addition in experiments grams	Average lime dosage kg/t
9.2	0	0
9.9	0.23	0.15
10.9	0.88	0.58
11.8	2.55	1.7
12.5	13.1	8.73

As explained by Bulatovic (2007) and Chettibi et al (2012), both the flotation and depression of iron and copper sulfide minerals is dependent on collector concentration as well as pH conditions, which, when controlled by lime, releases calcium Ca^{+2} and OH^{-}. On one hand, OH^{-} forms the surface complexes that allow a sulfide mineral to float at the right conditions. On the other hand, it is the concentration of Ca^{+2} and their adsorption onto the mineral surface that result in the depression of the mineral particles. It was found that above pH 12, chalcopyrite depresses significantly, along with pyrite and pyrrhotite, which help to explain the results found in test number 13.

The best recovery for copper was obtained from the first run at collector dosage of 42.9 g/t, depressant dosage of 80.7 g/t and pH of 9.9. This goes well in accordance to previous research work done on the studied ore as well as a close similarity with current operating conditions on site. In contrast, excluding the previously discussed results on test number 13, the next lowest performance was found in test number 8, which was performed at collector dosage of 22.1 g/t, depressant dosage of 24.3 g/t and pH of 11.8. Again, the low recovery seemed to be strongly affected by the high pH level.

The six center runs, performed at constant values for error estimation were satisfactorily consistent in terms of copper recovery. With a collector dosage of 32.5

g/t, depressant dosage of 52.5 g/t and pH of 10.85, an average copper recovery of 83.5 %. At this point of the analysis, it is noticeable that pH is the strongest influencing variable in the copper recovery response when the system is described by the selected variables within the chosen operating region.

8.1.1.2 Copper grade % in concentrate and enrichment ratio

Similarly to copper recovery, the lowest value was found from run number 13, strongly influenced by pH, as explained previously, and yielding a result of 6.9%. The next lowest value was found at run number 2, which, in accordance with the typical behavior of a recovery against grade curve, at a relatively high recovery of 83.9%, grade was low at 7.27%. Since copper grade depends on which other minerals have floated, and their concentration relative to the copper minerals in the concentrate product affects the ultimate copper yield achieved, there are an important number of drivers for this occurrence. At a pH as low as 9.9, and by analyzing the iron recovery in this test, it is believed that copper grade suffered due to insufficient pH conditions to depress the iron minerals, causing a decrease in copper grade even greater than other tests performed at higher pH and similar collector and depressant dosages.

Other reasons for low copper grades can be explained by the scale at which laboratory experiments for batch flotation are performed. Physical factors such as slurry and froth levels (heights) and cell geometry can ultimately result in increased entrainment (particle-liquid) and entrapment (particle-particle) effects that increase the amount of hydrophilic particles (e.g., iron minerals), thus affecting positively iron recoveries and grades. Such an effect is thought to differ at an industrial scale, since higher slurry and froth levels allow for proper dynamics in which mostly properly attached hydrophobic particles leave through the froth. Frother additions were constant through all experiments and only in administered in conditioning stage, contributing to steady degradation of the froth, which is contrary to continuous flotation at plant level, where frother is compensated for in order to maintain froth quality. Additionally, most modern cell and flotation circuit designs

include launder stages, in which undesired particles are removed from the froth after flotation stages prior to the next operation in the process. (Napier Munn and Wills, 2007)

In center runs, a higher variation was found in copper grade than copper recovery. Some of the previously explained reasons are believed to drive this behavior. While the highest copper grade was found in test number 5, at a relatively high pH of 11.8 as well as high depressant dosage of 80.7 g/t. Conversely, the recovery for such test was low at 74.5%, obeying the recovery-grade relationship and possibly aided by the depressing effect of the gangue due to a high depressant dosage.

Regarding enrichment ratio, the lowest value of 14.8 was found in test number 13, consistently with the previous two responses. An average value of 18.5 was attained from all the tests, with a maximum value of 24 from test number 5, a factorial point with a copper recovery of 74.9%. In general, for low grade ores (below 1% Cu), undergoing only one stage of concentration (rougher flotation), enrichment ratios of above 10 are considered within the acceptable range, meaning that the grade by mass of copper has increased over ten times (Napier Munn and Wills, 2007; Grönstrand et al, 2011). Therefore, all of the results obtained in the first experimental phase are deemed as normal and within standard spectrum of recoveries and grades, comparable to previous studies and industry in general.

8.1.2 Iron and nickel grades and recoveries

8.1.2.1 Iron grade and recovery

Iron grades showed great consistency in tails and concentrate. Tails presented an average Fe grade of 9.6% with standard deviation of 0.14%, while concentrate grades averaged 18% with standard deviation of 1.44%. The lowest concentrate grade value for iron was observed in test number 13 at a value of 13.9%, consistently with the previously reported results from copper. A maximum value of 20.8% was observed in test number 10, a factorial point that showed relatively high copper and nickel grades, which can explain the high iron value. While center points

seemed to generate sufficiently consistent iron grades, this consistency was not carried onto recovery results, where high level of variance was found that complicated the proper statistical analysis and selection of model.

Recoveries ranged from as low as 0.8% in center point and test number 3 to 12.3% in axial point and test number 20. The lowest seems inconsistent with copper and nickel recoveries sufficiently high to consider that iron would be represented as well due to shared mineralogy. Therefore, the low result could be attributed to experimental error in the assay stage for this particular test and metal. On the other hand, the studied process variables did not seem to greatly affect iron recovery beyond a strong pH influence, as it has already been explained by the literature review. The large inconsistency in the recoveries is considered due to the different recoveries of both copper and nickel minerals, as well as previously mentioned experimental conditions such as cell volume, slurry and froth level and lack of launder as in an industrially scaled process. However, the main reason for inconsistencies is believed to be due to the fact that the selected variables are thought to be more influential for copper recovery and both iron grade and recovery could be better controlled by other variables, which would generate enough quality data to proper model its behavior in the system.

8.1.2.2 Nickel grade and recovery

As agreed for this study, nickel grade and recovery do not represent high priority targets at the operating site. Since nickel is a desirable product on its own, it is allowed to flow onto copper cleaning stages, where, at lower mass quantities, pH and reagents can be properly adjusted and dosed in order to have a highly effective separation from the main copper concentrate. In spite of this approach, it was considered worthwhile to collect the responses in terms of grade and, for modeling purposes, recovery for nickel. The results, while more consistent than iron, were not as consistent as with copper. This is also believed to be due to the lower correlation between the selected variables when compared to copper.

Nickel grades and recoveries were markedly lower than copper ones. This was expected and desired, since, although similar in behavior to chalcopyrite, pentlandite is effectively floated under pH conditions of 9.5 and below. Nickel and nickel-copper ores generally produce low concentrate grades in spite of high recoveries. With grades rarely going above 15% and usually around 6%, and recoveries well around 90%, the results obtained for nickel fall under this behavior. (Bulatovic, 2007)

In accordance to copper and iron grades, the lowest nickel grade was result of test 13 at 0.4%, however, the lowest recovery was observed in test number 2 with 9.6%. Grades ranged between 0.4% - 3.5%, which is in agreement with Bulatovic (2007). The average grade for nickel center runs was 1.7% with high replicability.

Nickel recoveries ranged between 9.6% - 58%, the highest of which was observed in test number 1, having also the highest grade observed. The highest recoveries for nickel were observed in accordance to theory, at pH values below 10. Nickel recoveries were sufficiently constant in center runs, giving a good sense of replicability for the modeling and prediction stage of nickel responses from the system.

8.2 Statistical modeling, optimization and confirmation of predictions

Up to this point, only a high level analysis of the results has been performed. It is important, before performing the necessary data processing and regressions to obtain the proper models, to verify that the results fall within previously studied and agreed behaviors for the minerals comprising the studied ore. Having done this, the present section of this chapter will utilize the data so far collected, generate the models, perform a thorough analysis of model properties, and exemplify the selection of optimization criteria, as well as the execution of confirmation runs to corroborate the accuracy of the optimization exercise within the confidence intervals defined by the system.

8.2.1 Copper recovery model

The first step towards building a regressional model for copper recovery is to ensure there is no co-linearity between any of the variables (factors), followed by determining the relative influence of each of these variables on the response, either negative or positive. Such task was performed by obtaining correlation matrixes as it is exemplified in Figure 20, where collector dosage has a positive correlation to copper recovery; depressant presents an almost negligible influence over it and pH displays the largest correlation in a negative way. These phenomena will later be corroborated in the model coefficients and the interaction effects of the variables.

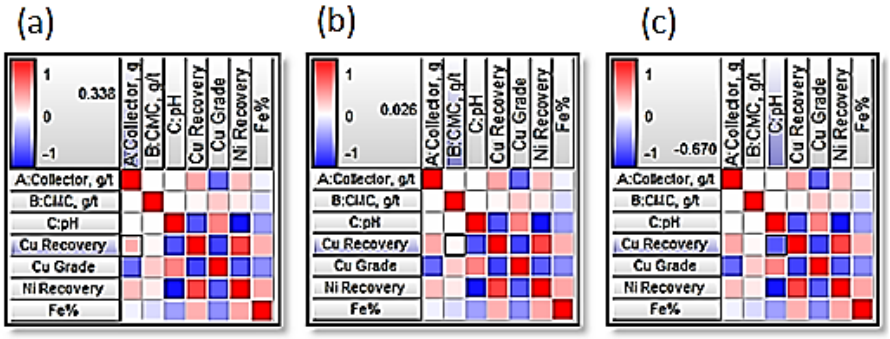

Figure 20. Correlation matrix for the system displaying the correlation values respect to copper recovery for (a) collector dosage at 0.338, (b) depressant dosage at 0.026 and (c) pH at -0.670.

The following step consisted in comparing the different models that could fit the results from the experiments; from linear, to quadratic with and without interactions as well as cubic models. Table 8 introduces the preliminary characteristics of the different models prior to variable elimination due to statistical significance, as well as data point elimination.

Table 8. Summary of model characteristics prior to ANOVA.

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0.0142	0.0005	0.4160	-0.0501	
2FI	0.9860	0.0003	0.2660	-0.8955	
Quadratic	0.0049	0.0018	0.7817	-0.4958	Suggested
Cubic	0.0006	0.1634	0.9939	0.3973	Aliased

As seen in the table, sequential p-value and lack of fit p-values indicate that the actual response and no noise are modeled using the quadratic model, as well as that there is no significant lack of fit, mainly due to the fairly repetitive values achieved in center runs. However, although a standard quadratic model is suggested, a predicted R^2 taking a negative value indicates that the mean value for the response would be a better choice for prediction than the model itself, deeming the model as presented non-useful. Taking this into account, a further ANOVA (Analysis of Variance) is presented in Table 9, where the significance of the selected terms is evaluated, as well as other model properties.

Table 9. ANOVA for first copper recovery quadratic model.

Source	Sum of squares	Degrees of freedom	Mean square	F Value	p-value Prob > F	
Block	17.71	2	8.85			
Model	1047.27	9	116.36	7.76	0.0042	significant
A-Collector, g/t	31.86	1	31.86	2.13	0.1830	
B-CMC, g/t	0.18	1	0.18	0.012	0.9148	
C-pH	573.76	1	573.76	38.27	0.0003	
AB	0.41	1	0.41	0.028	0.8722	
AC	0.71	1	0.71	0.048	0.8326	
BC	5.88	1	5.88	0.39	0.5486	
A^2	0.17	1	0.17	0.011	0.9184	
B^2	1.61	1	1.61	0.11	0.7512	
C^2	418.62	1	418.62	27.92	0.0007	
Residual	119.93	8	14.99			
Lack of Fit	119.15	5	23.83	91.02	0.0018	significant
Pure Error	0.79	3	0.26			
Corr. Total	1184.91	19				

Perhaps the main indicator that the model is not adequate for a prediction is given by the fact that, although the model is rendered as significant, at this point only pH and the squared value for pH are significant. As previously stated, only lack of fit points help adjust the prediction to the actual values. At this point, a viable course of action is to find outliers in the dataset as well as highly influencing points that might not allow the surface to properly map the response. First, an analysis of studentized residuals is performed from a plot of residuals as shown in Figure 21.

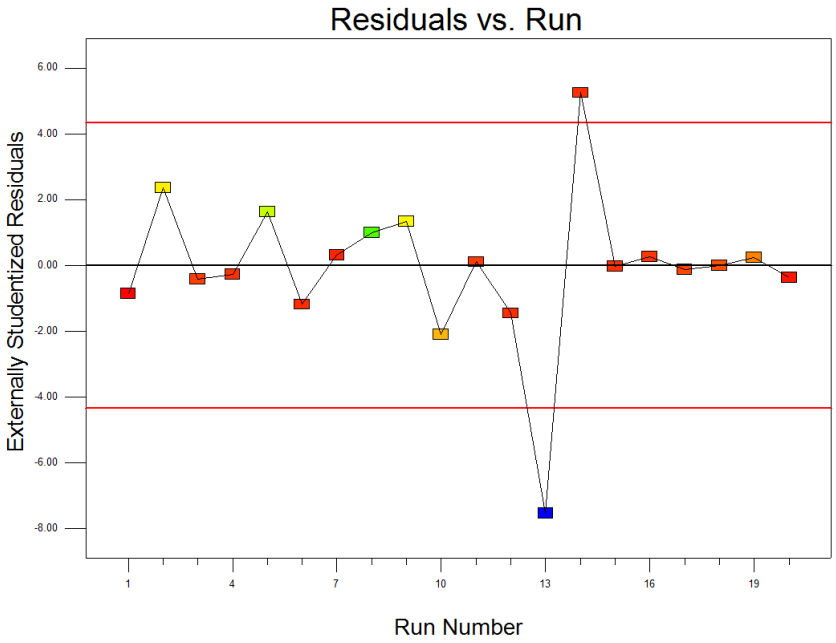

Figure 21. Plot of residuals for the first copper recovery model.

According to the hypothesis, run 13 is considered an outlier by being the largest residual out of threshold limits. The elimination of this point from the dataset represented a big improvement, mostly by shifting the predicted R^2 to a value of 0.153. This still is insufficient, but clearly on the right direction, as shown in Figure 22.

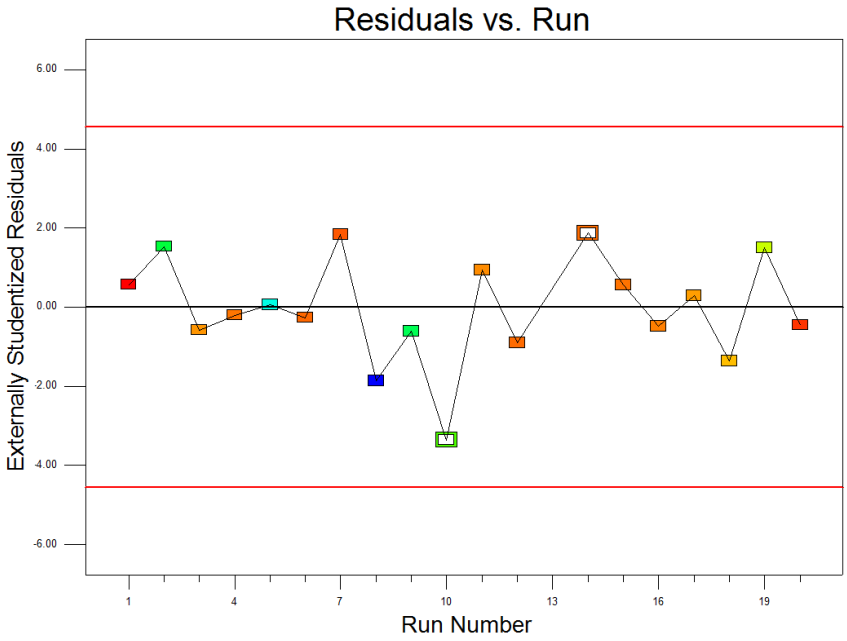

Figure 22. Plot of residuals for second copper recovery model.

As it can be seen, no more clear outliers are present in the response judging merely by the residuals. However, as highlighted in Figure 22, runs number 10 and 14 still present the largest residuals. By performing a cross analysis with a Cook's Distance plot, which highlights the relative magnitude that the elimination of a data point would have on the regression as well as a Difference of Fits plot, providing a sense of which point have the greatest influence on overall lack of fit between model predictions and actual values if eliminated. Both plots are represented in Figure 23, which points to the elimination of Run number 10, since it equally represents a greater residual, high effect on regression from elimination and influence on the fit (lack of fit) of the model to actual results.

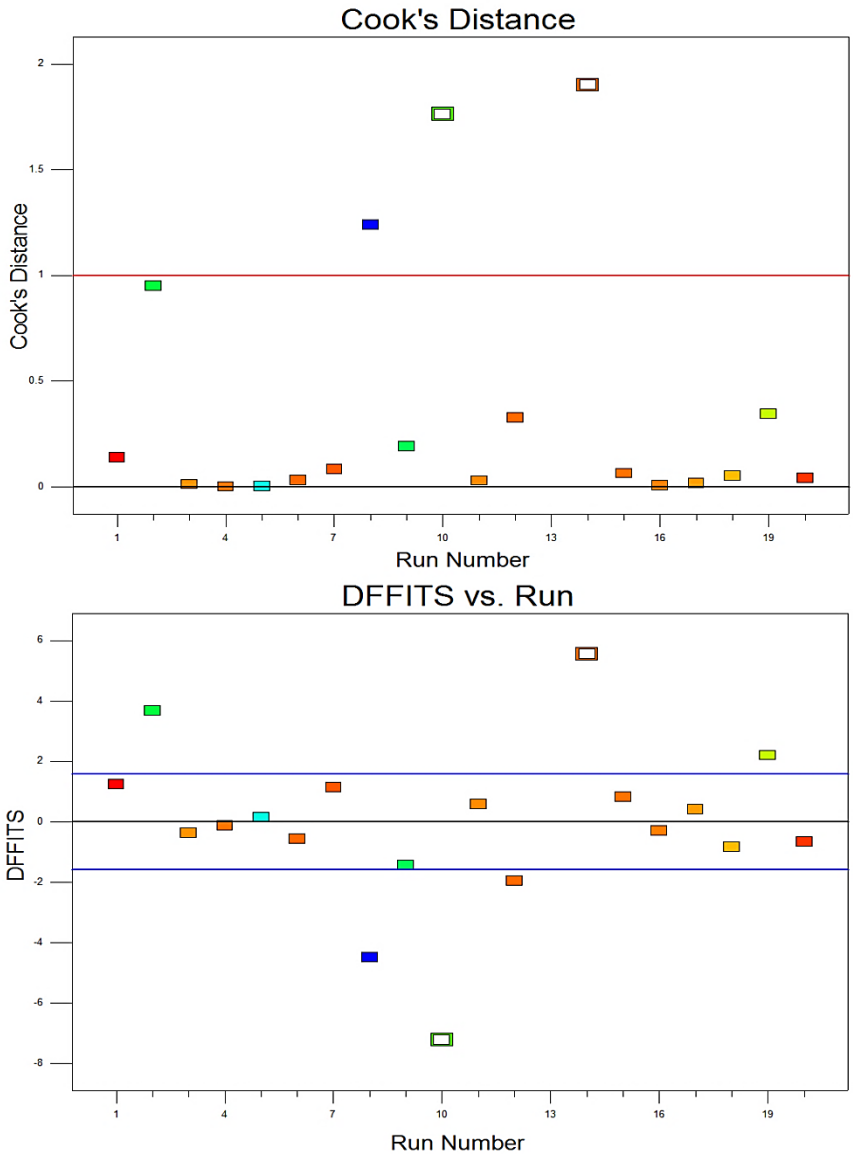

Figure 23. Cook's distance and DFFITS plots to aid in identification of influencers to the model.

A relatively large effect after elimination, according to Cook's distance, and the largest influence on lack of fit, reveals run number 10 as the choice to be ignored from the dataset in order to achieve a better regression model.

An analysis of variance (ANOVA) was performed in order to select the final significant variables, as well as to evaluate the final model properties. The final ANOVA results of the copper recovery model for the system are presented in Table 10.

Table 10. Final Analysis of Variance Results (ANOVA) for copper recovery model.

Source	Sum of squares	Degrees of freedom	Mean square	F value	p-value Prob > F	
Block	34.83	2	17.42			
Model	232.45	6	38.74	58.70	< 0.0001	significant
A-Collector, g/t	10.75	1	10.75	16.28	0.0030	
B-CMC, g/t	4.98	1	4.98	7.54	0.0226	
C-pH	184.33	1	184.33	279.28	< 0.0001	
AB	2.96	1	2.96	4.48	0.0633	
AC	8.96	1	8.96	13.57	0.0050	
C^2	73.73	1	73.73	111.72	< 0.0001	
Residual	5.94	9	0.66			
Lack of Fit	5.15	6	0.86	3.28	0.1786	not significant
Pure Error	0.79	3	0.26			
Cor Total	273.22	17				

The final copper recovery model resulted in a modified quadratic with main effects of the variables, collector-depressant interaction, collector-pH interaction as well as the pH quadratic effect. By obtaining the ratio between the model mean square and the model residual, an F-value of 58.7 is sufficiently big compared to the critical F-value of 3.37, which is required for the available degrees of freedom of the model and residual of 6 and 9 respectively, therefore rendering the model significant. As demonstrated by the p-test, there is only a 0.01% chance that this is due to randomness. The ratio between lack of fit error and pure error yields a value of 3.28, lower than the critical F-value between these two parameters of 8.94, therefore lack of fit is non-significant. All critical F-values for 95% significance used for the ANOVA of all models of this study can be found in Appendix 1.

The model presents an R^2 value of 0.975, adjusted R^2 of 0.958 and a predicted R^2 of 0.81; all good characteristics for explaining the quality of the model as it captures enough of the variance and presents good prediction properties for optimization.

The final models with coded variables (unitless values ranging from -1 to 1), as well as with actual variables (with coefficients adjusted to fit their real units), are presented in Table 11.

Table 11. Copper recovery model equations for coded and actual variables.

Coded variables		Actual variables	
Coefficient	**Variable**	**Coefficient**	**Variable**
+83.25		-198.7	
+0.98	A	-1.1	Collector, g/t
+0.67	B	+0.1	CMC, g/t
-5.15	C	+59.6	pH
-0.71	AB	-2.4E-3	Collector*CMC
+1.24	AC	+0.1	Collector*pH
-3.05	C^2	-3.2	pH^2

Both models can be used for prediction of the response. However, only the first model can be used for an estimation of the relative effects of the process factors and the interaction effects, since in the second model the coefficients are modified to account for the differences in magnitude and units of the factors they represent. A predicted against actual plot is presented in Figure 24 to show the reasonable agreement between experimental results and model predictions.

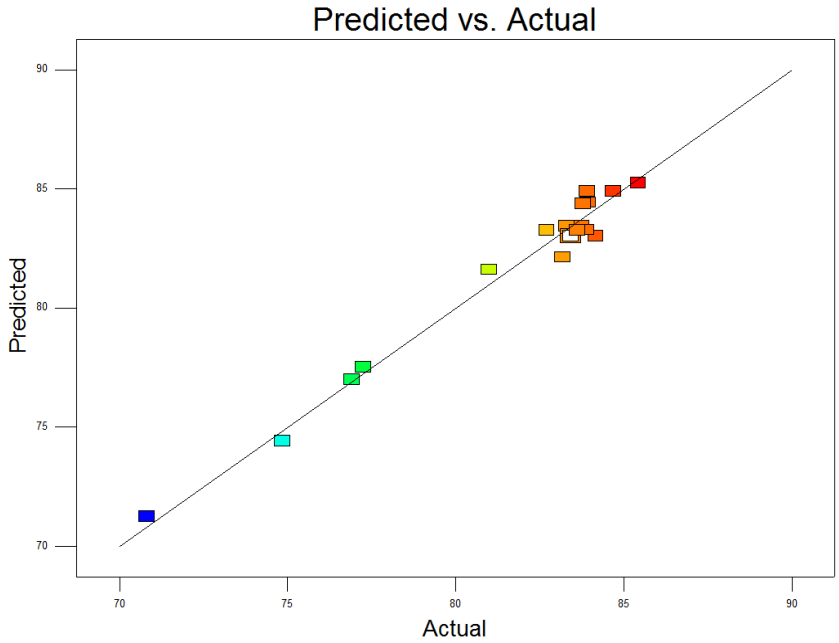

Figure 24. Predicted against actual plot for copper recovery model.

Lastly, Figure 25 shows the response in contour projections as well as three-dimensional surfaces for low, medium and high pH values. Although at this point it is clear where a maximum value region would be, it is important to obtain the rest of the models in order to define the optimization criteria and evaluate whether or not a solution is feasible and desirable.

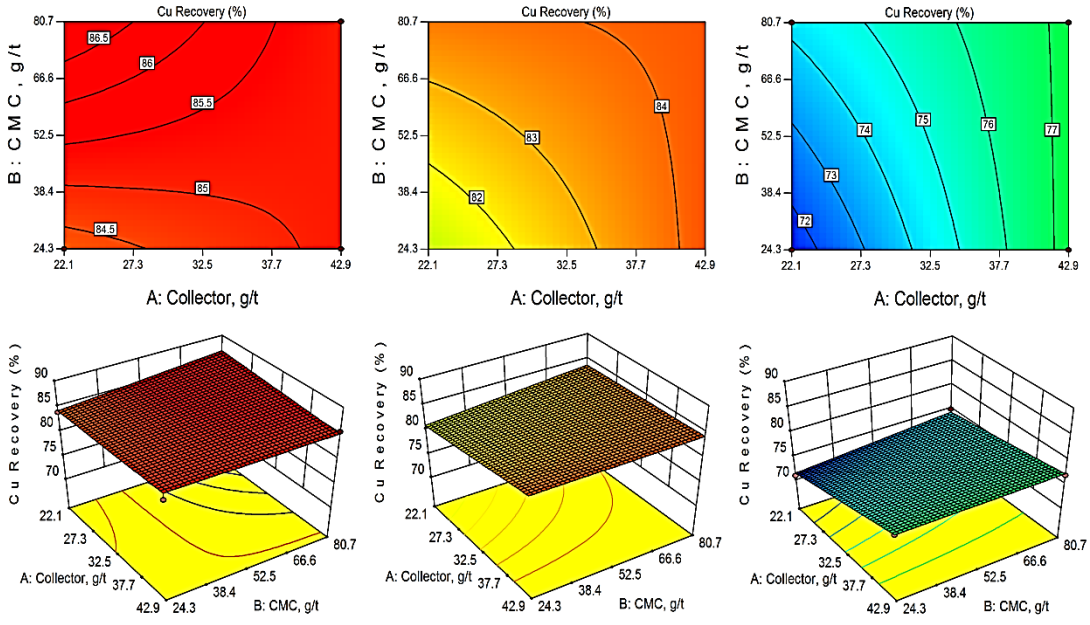

Figure 25. Copper recovery contour and surface plots at conditions of (a) low pH (9.8), (b) medium pH (10.85), and (c) high pH conditions (11.8).

It becomes clear how pH is the variable that bears the highest influence on copper recovery, with collector and depressant concentrations playing a smaller positive role in recovery. Regarding the interaction effect between collector and depressant, it is observable to be negative as clearly seen previously in Table 11, which is the cause for the tilting of the surfaces near the limits of the represented space.

Even though it is apparent that lower pH conditions within the operating region are beneficial to copper recovery, the development of the rest of the models and their respective surfaces will support a more balanced optimal point by taking their responses into consideration.

8.2.2 Copper grade model

A model for copper grade of the rougher concentrate was obtained in a similar way as for copper recovery. As previously explained, it was more difficult to properly model grade as a response of the same system with the same variables due to lower correlation between it and the variables. Nevertheless, it was considered worthwhile to generate a model that would provide a prediction of grade to a certain extent. The results from the final ANOVA properties are presented in Table 12 followed by the coded and actual model equations in Table 13.

Table 12. Final Analysis of Variance Results (ANOVA) for copper grade model.

Source	Sum of squares	Degrees of freedom	Mean square	F value	p-value Prob > F	
Block	3.81	2	1.90			
Model	12.31	3	4.10	33.89	< 0.0001	significant
A-Collector, g/t	3.59	1	3.59	29.64	0.0001	
C-pH	7.40	1	7.40	61.13	< 0.0001	
C^2	0.76	1	0.76	6.27	0.0278	
Residual	1.45	12	0.12			
Lack of Fit	0.65	9	0.073	0.27	0.9435	not significant
Pure Error	0.80	3	0.27			
Cor Total	17.57	17				

As demonstrated by the ANOVA results, the best fitting model for copper grade did not consider any interactions between variables. Also, based on p-test results, it does not consider the depressant dosage as significant, leaving only the depressant

dosage and pH as the descriptive variables for the response. The ANOVA results determine that the model presented in Table 13 is significant with very low probability that this significance has occurred randomly. The F value of 33.89 is larger than 3.86, which represents the critical F-value for model significance. The ratio between the pure error and lack of fit is smaller than critical F value of 8.89 at 0.27; therefore there is no significant lack of fit of the model in respect to the data. This however contrasts with a large p-value for lack of fit of 0.9435, which strongly suggests that such property could be purely random. The model presents an Adjusted R^2 value of 0.868, which is considered appropriately large for explaining the error by the model.

Table 13. Copper grade model equations for coded and actual variables.

Coded variables		Actual variables	
Coefficient	Variable	Coefficient	Variable
+8.59		+37.27158	
-0.54	A	-0.051912	Collector
+0.98	C	-5.97585	pH
+0.31	C^2	+0.32145	pH^2

A predicted against actual plot is presented in Figure 26 where, although it is apparent there exists relatively greater error when compared to the previous recovery model, there is enough evidence that the overall effects of the predicting variables can be used to predict behavior.

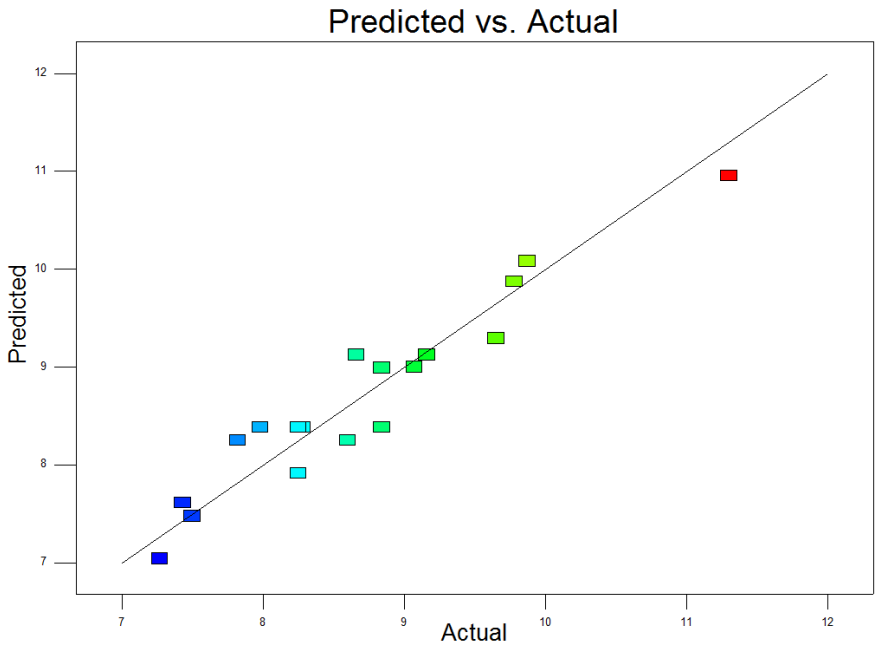

Figure 26. Predicted against actual plot for copper grade model.

The contour and surface plots for copper grade are introduced in Figure 27. Here, it can be corroborated that there is an opposite behavior to pH conditions in flotation compared to the recovery response. It is important to note that copper grade is not a response to be optimized in this case study, but rather a reference response used to account for congruence in the experiments in contrast with the observed values and behaviors displayed by the model. In this case, pH is the strongest influencing variable, at the same time that increasing the collector dosage seems detrimental to copper grades.

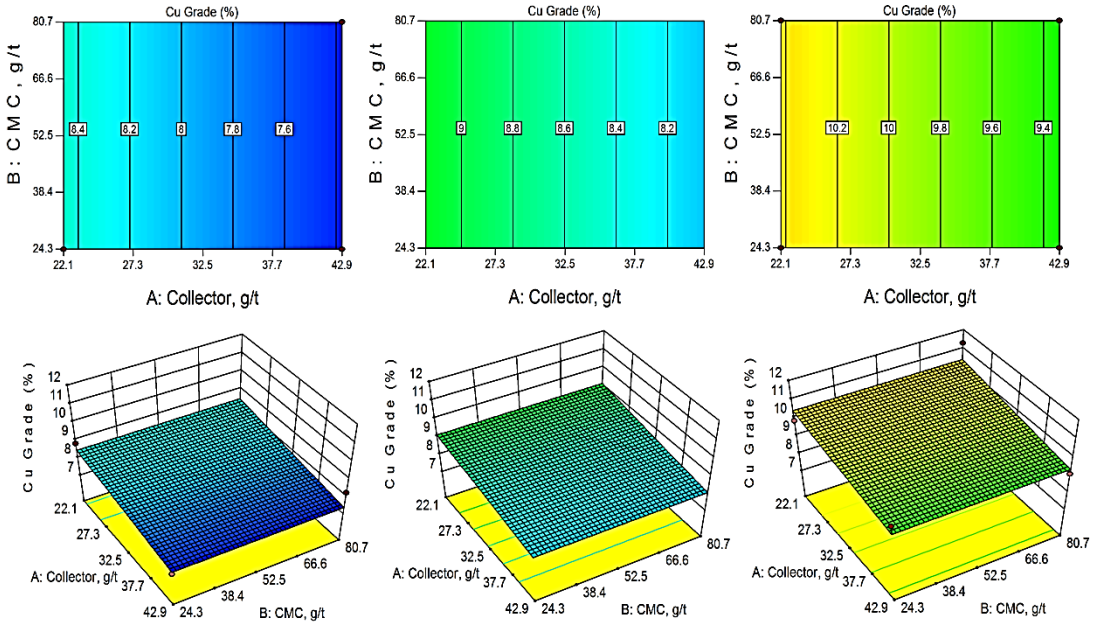

Figure 27. Copper grade contour and surface plots at conditions of (a) low pH (9.8), (b) medium pH (10.85), and (c) high pH conditions (11.8).

8.2.3 Iron recovery model

The model for iron recovery was obtained from the system in a similar way as for copper recovery and grade. This however proved to be the least accurate of the four models, and based on the results from the ANOVA, it cannot be utilized for predictions. The results of the ANOVA are shown in Table 14.

Table 14. Final analysis of variance results (ANOVA) for iron recovery model.

Source	Sum of squares	Degrees of freedom	Mean square	F Value	p-value Prob > F	
Block	30.98	2	15.49			
Model	24.68	8	3.09	3.05	0.1175	not significant
A-Collector, g/t	0.10	1	0.10	0.099	0.7652	
B-CMC, g/t	5.01	1	5.01	4.95	0.0766	
C-pH	4.39	1	4.39	4.33	0.0919	
AB	6.65	1	6.65	6.57	0.0505	
AC	7.22	1	7.22	7.13	0.0443	
BC	8.77	1	8.77	8.66	0.0322	
B^2	5.53	1	5.53	5.46	0.0666	
C^2	4.57	1	4.57	4.52	0.0869	
Residual	5.06	5	1.01			
Lack of Fit	2.50	3	0.83	0.65	0.6522	not significant
Pure Error	2.56	2	1.28			
Cor Total	60.73	15				

The model presents no significance in terms of how closely it could model the response. It was obtained after eliminating highly problematic data points (experimental runs) besides runs number 10 and 13 as with the previous models, it was also necessary to get rid of factorial run number 2 and central run number 4 due to the high residuals and influence on the model's inability to adjust to the natural curvature of a recovery.

An F value of 3.05 is smaller than the critical F value of 4.81 required for model significance. This shows a poor ability of the model to explain the variance from the mean response. Since there is a fairly similar value for pure error recorded from the center runs and the lack of fit measurements with an F value of 0.65 lower than critical value of 19.16, there is no significant lack of fit; however these values are fairly larger than the previous two models, at a low response spectrum.

The model was chosen to be a quadratic model, which goes in accordance to previously studied cases from the literature (Rath et al., 2013). The value for R^2 is at 0.83 and the adjusted R^2 is at 0.55. In spite of large R^2 values, there is enough evidence to avoid the use of this model as a predictor for any future runs and that such high values are largely due to the reduction of data points and therefore a high R^2 value can be just due to the higher complexity of the model.

There is, however, a possibility to analyze the contour and surface plots, as the predictors chosen for the model equations present enough significance to understand the average trends occurring from varying the variables values. As explained by Frost (2013), even a non-accurate model for prediction (e.g., no significance due to large error) can be used to understand the behavior of the response in the system if the predictors are significant, as shown by the ANOVA results, with the exception of A, which is far from a p value of 0.05.

As previously discussed, one hypothesis for the difficulties encountered in trying to model the iron recovery response could be due to the complexity of the mineral body, where Iron is present in almost every other mineral containing the copper

and nickel species such as chalcopyrite and pentlandite, in addition to pyrrhotite. One way in which this problem could be overcome in future studies would be to measure a proxy response, such as the recovery of the highest iron bearing mineral instead of the element iron, which introduces too much variance in the recorded data.

Another approach would be to study further the liberation size for different copper minerals in order to reduce the variability in the results of both copper and iron grades and recoveries. This approach, however, was not part of the scope for the current case study and hence was ruled out from the experimental design. The model coefficients and variables are presented in Table 15.

Table 15. Iron Recovery model equations for coded and actual variables.

Coded variables		Actual variables	
Coefficient	**Variable**	**Coefficient**	**Variable**
+8.41		-127.4	
+0.11	A	+2.4	Collector
-0.75	B	-1.4	CMC
-1.03	C	+25.6	pH
+2.62	AB	+8.9E-3	Collector*CMC
-2.73	AC	-0.27	Collector*pH
+3.01	BC	+0.1	CMC*pH
-0.72	B^2	-9.0E-4	CMC^2
-1.05	C^2	-1.1	pH^2

As it can be seen from the model coefficients, there is a positive effect of the collector addition on iron recovery; however it becomes counterbalanced by increasing pH values, which have stronger influence on iron flotation. Depressant shows a negative effect on iron recovery, as it would be expected. Depending on the collector and depressant dosages, the recovery can increase at given pH levels until reaching a peak and falling again, as it will be demonstrated in Figure 29. Figure 28 presents the predicted against actual plot for iron recovery.

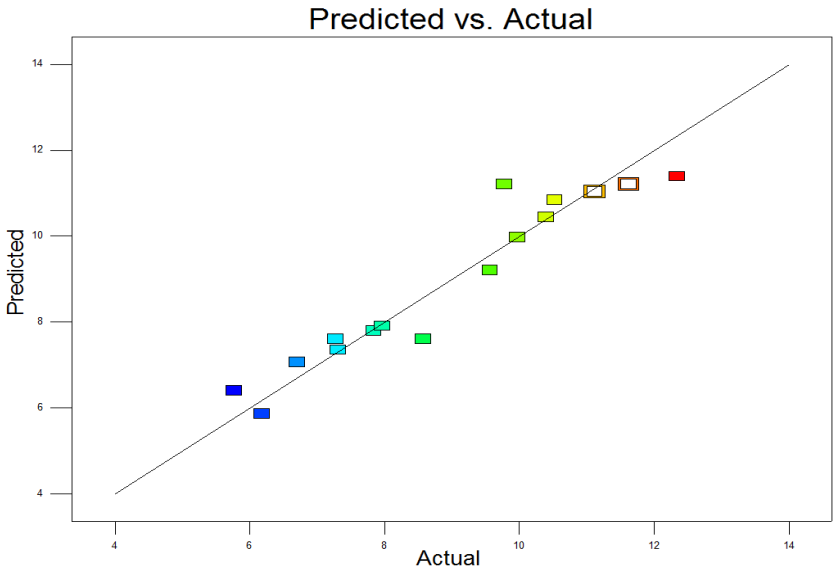

Figure 28. Predicted against actual plot for iron recovery model.

The predicted against actual plot does not bring much information other than demonstrating that the larger variance is found at the center values between 8% and 10% of recovery for iron.

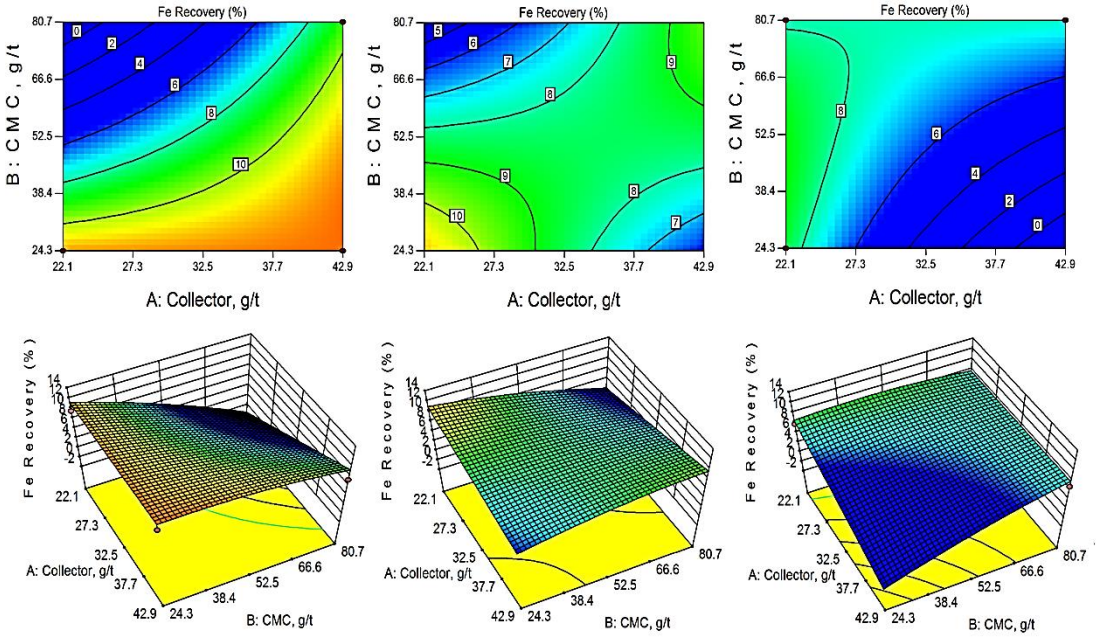

Figure 29. Iron recovery contour and surface plots at conditions of (a) low pH (9.8), (b) medium pH (10.85), and high (c) pH conditions (11.8).

As shown by the above figure, there is a noticeable saddle-like behavior in the response, especially around the center experimental conditions of pH 10.85. It can

be clearly seen that as pH levels continue rising, iron recovery drops further even at high collector dosage, which can be a key for the later optimization of copper recovery. Overall, it should be important to keep pH values beyond 10, in order to not sacrifice too much of copper recovery and to expect low iron recoveries.

8.2.4 Nickel recovery model

The last of the models was for the recovery of nickel. In contrast to Iron recovery, the nickel recovery response was able to be modeled significantly, however with lesser attributes in the model than those observed for the copper recovery. This is believed to be due to the presence of nickel mostly on pentlandite, contributing to a lesser dispersion of the metal in minerals, but low causation from the selected variables to model the response. The results from the ANOVA are presented in Table 16.

Table 16. Final analysis of variance results (ANOVA) for nickel recovery model.

Source	Sum of squares	Degrees of freedom	Mean square	F value	p-value Prob > F	
Block	54.81	2	27.41			
Model	3402.85	6	567.14	64.81	< 0.0001	significant
A-Collector, g/t	221.53	1	221.53	25.32	0.0005	
B-CMC, g/t	22.78	1	22.78	2.60	0.1377	
C-pH	2989.01	1	2989.01	341.58	< 0.0001	
AB	65.14	1	65.14	7.44	0.0213	
AC	96.01	1	96.01	10.97	0.0078	
BC	8.38	1	8.38	0.96	0.3510	
Residual	87.51	10	8.75			
Lack of Fit	53.57	7	7.65	0.68	0.6990	not significant
Pure Error	33.94	3	11.31			
Cor Total	3545.17	18				

A two factor interactions model was selected for nickel recovery. As it can be seen from the ANOVA results, the model is significant with a fairly large F value of 64.81 compared to a critical F-value required of 3.13, indicating that a good amount of the variance is explained by the model with low chance of it being due to randomness (less than 0.01%). All linear terms, with the exception of the depressant are significant; however this was kept for respecting hierarchy of the model for the interactions. There is no significant lack of fit and the F value is fairly small and well

within the ranges of that for the copper recovery model, therefore, the surface correctly fits the response within the space of the design.

The model presents R^2 value of 0.97 and the adjusted R^2 is at 0.96 and a prediction R^2 of 0.9. Therefore, the model can be used for understanding the average behavior of the response as well as for predictions in subsequent experiments since it presents significant variables and not as many data points were ignored as in the previous models (only run number 13). The coefficients of the model are presented in Table 17.

Table 17. Nickel recovery model equations for coded and actual variables.

Coded variables		Actual variables	
Coefficient	Variable	Coefficient	Variable
+28.27		+118.5	
+4.03	A	+3.6	Collector, g/t
+1.29	B	-0.7	CMC, g/t
-16.93	C	-8.2	pH
+2.85	AB	+9.7E-3	Collector*CMC
-3.46	AC	-0.3	Collector*pH
+1.02	BC	+0.04	CMC*pH

When compared to the coefficients of copper recovery, it becomes clear that nickel recovery follows a very similar behavior. Most of the primary effects follow the same trend with a lesser adjustment of the constant due to the lower recoveries that naturally happen for nickel. pH has greater effects on nickel than it has for copper, and depressant and collector have a similar positive effect with lower strength on it.

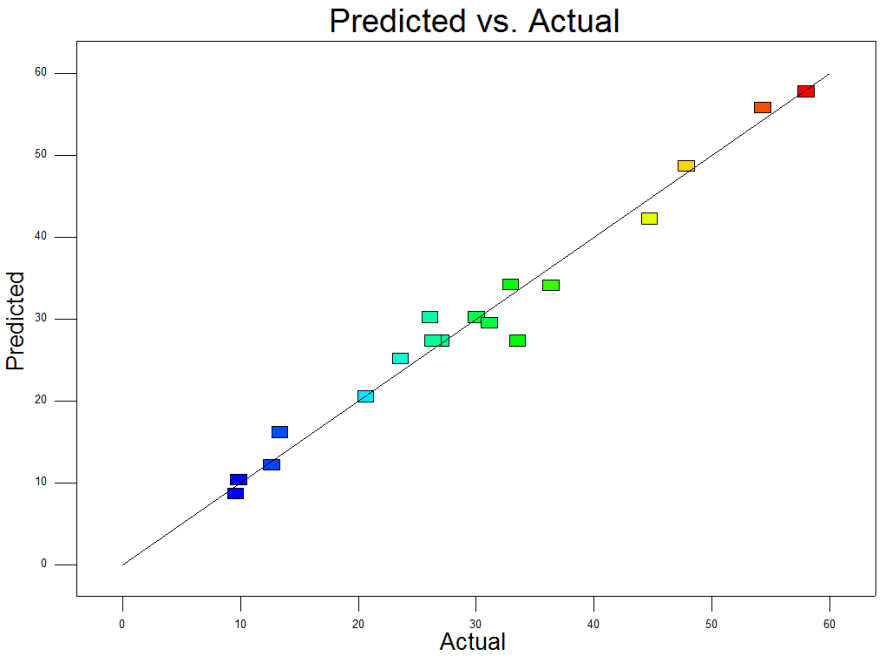

Figure 30. Predicted against actual plot for nickel recovery model.

The predicted against actual plot in Figure 30 reveals a fairly close approximation between the results and the model, with a slight deviation around 30% recovery, however not so strong. The surfaces and contours are presented in Figure 31.

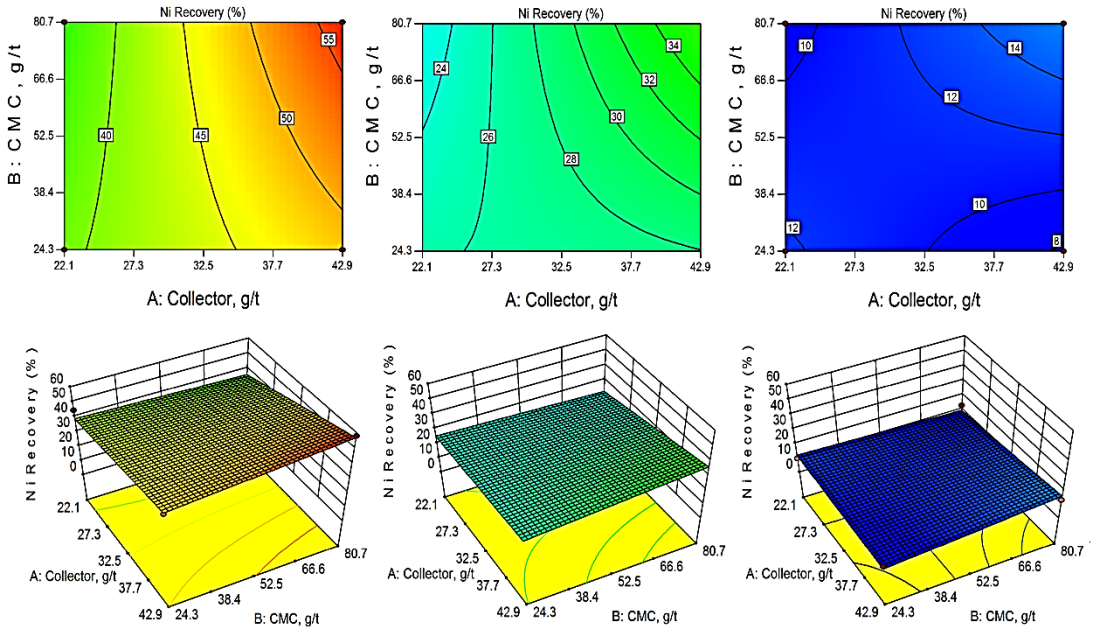

Figure 31. recovery contour and surface plots at conditions of (a) low pH (9.8), (b) medium pH (10.85), and (c) high pH conditions (11.8).

The figure above reveals the fact that the two factor interaction model for nickel presents a strongly similar shape and behavior as the one for copper recovery. This is especially apparent in the surface plots where it can be seen that a possible control recovery for nickel could sit between 20% and 30%. Although this is not a response to be optimized, such information in a model can be used for recovery predictions, enabling the operating staff to plan downstream operations such as cleaning, as well as adjustment of process variables in the nickel flotation stage.

8.3 System optimization

8.3.1 Optimization objectives

The models obtained in the previous section were utilized to perform the optimization of the rougher flotation system for copper. The technique utilized was the one of superimposition of response curves as presented by Myers et al. (2009). This technique is particularly useful because of its simplicity to combine the response curves in one plot and differentiate between the feasible and unfeasible regions according to the optimization parameters set as goals. The values selected to be met by the 4 responses are presented as follow in Table 18.

Table 18. Optimization criteria.

Response	Minimum value, %	Maximum value, %
Copper recovery	82	85
Copper grade	7.27	11.3
Iron recovery	5.8	12
Nickel recovery	20	40

The primary objective of the optimization was to maximize copper recovery while keeping nickel recovery at reasonable levels between 20% and 35% in order to minimize the usage of reagents for the cleaning stages and to have a more stable rougher product. The copper grade was kept within range of the observed response and therefore acts only as an informative parameter in the optimization. Iron recovery, due to the poor properties of the model is also considered as informative and it was used to control the decision of dosages and pH selected as optimal. In other words, solutions at pH lower than 10.8, with high dosages of collector and low dosages of depressant, or low dosages of both reagents, were avoided due to the observable tendency of resulting in higher iron recoveries at such settings. Figure 32 presents the superimposed plot of responses with clearly defined feasible regions that meet the optimization parameters previously discussed.

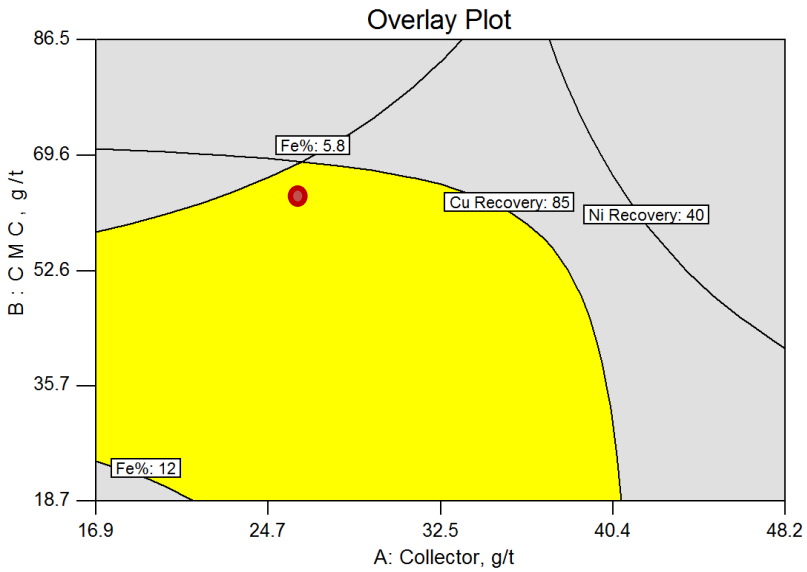

Figure 32. Superimposed plot of responses at pH 10.5 showing the contours for the different functions and feasible regions.

After analyzing the superimposed plot of responses shown in Figure 32, a clear solution around collector dosage of 26 g/t and depressant dosage around 65 g/t becomes apparent. However, before deciding to run confirmation tests at such values of the factors, it is important to analyze the standard error of the copper recovery model in order to have a sense of which areas should be avoided to base predictions on. Figure 33 presents the standard error distribution for copper recovery.

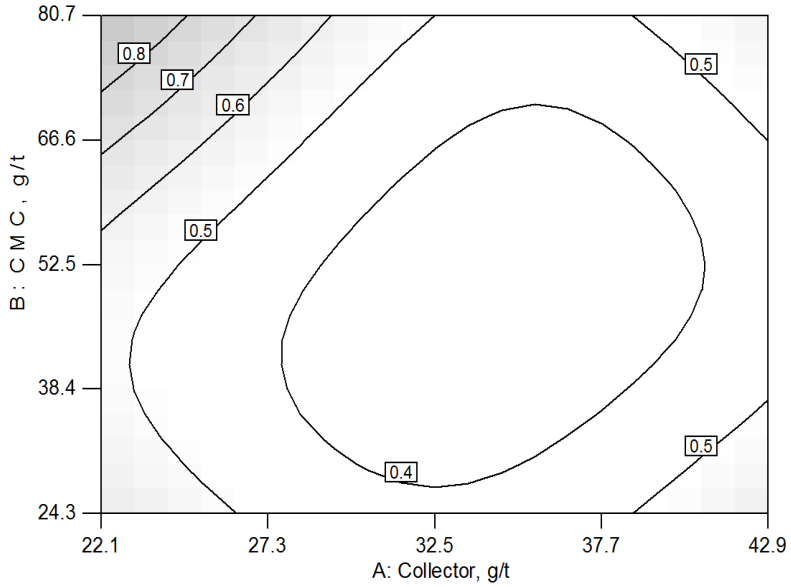

Figure 33. Standard error distribution for copper recovery.

A solution was selected at pH value of 10.5, collector dosage of 26 g/t and depressant dosage of 65 g/t. This solution would be located on a region of standard error distribution of 0.5, which is quite acceptable for confirmation runs of predictions. (Anonymous 2, 2013)

8.3.2 Confirmation tests

In order to correctly assess the confidence that can be given on the selected optimal solution, a total of three confirmation tests were performed at equal values for pH, collector and depressant dosages. Following the tests, the responses were recorded and the average of each was compared to the confidence, tolerance and prediction intervals in order to corroborate whether the objectives were met and how accurate predictions are possible to be attained by the models in practice.

Some design rules (Steele, 2014) call for a greater number of confirmation runs, however, in this particular case that possibility was not considered due to limitations in the availability of ore with similar characteristics. The selected point predictions, along with confidence and tolerance intervals at 95% confidence are presented in Table 19 as follows:

Table 19. Optimal point predictions with confidence and tolerance intervals for the four responses.

Response	Predicted mean	Predicted median	Observed	Standard deviation	SE mean	95% CI low	95% CI high	95% TI low	95% TI high
Cu recovery	84.9	84.9	-	0.81	0.45	83.8	85.9	81.8	87.9
Cu grade	8.6	8.6	-	0.35	0.14	8.3	8.9	7.5	9.7
Fe recovery	6.3	6.3	-	1.00	0.93	3.9	8.7	1.0	11.6
Ni recovery	30.8	30.8	-	2.95	1.01	28.6	33.0	21.4	40.2

The predicted mean represents the values observed in the superimposed plot of responses, indicating an expected mean copper recovery of 84.9%, copper grade of 8.6%, iron recovery of 6.3% and nickel recovery of 30.8%. However, these results are bound to model quality, associated error of the model and an estimation of confidence and tolerance intervals.

As explained by (Anonymous, 2012), the confidence interval represents the ranges in which 95% of the response results from similar experiments sampled at the optimal conditions would be contained. A confidence interval is not recommended to be used alone for a prediction; it is rather a measurement of sampling error.

For prediction purposes, it is important to look into the tolerance interval. This interval represents broader ranges, due to the inclusion of the uncertainty of the models. In Table 19, and considering only the copper recovery response, the tolerance intervals indicate that a 90% of a future population of experiments performed at selected optimal conditions will result 95% of the times in values between 80.6% and 89.1% recovery. The results from the three confirmation tests are presented in Table 20.

Table 20. Results from the confirmation tests at selected optimal point.

Test number	Cu recovery %	Cu grade %	Fe recovery %	Ni recovery %
1	81.6	10.3	6.9	40.4
2	83.8	8.45	6.7	37.4
3	81.7	8.74	5.6	37.4
Mean	**82.4**	**9.16**	**6.4**	**38.4**

As can be seen, copper recovery results, the primary objective for the optimization, were relatively far from the expected mean value of 84.9%. However, the three results, and their mean are within the tolerance interval, which, although quite broad, indicates that the confirmations responded to the prediction capabilities of the models for the selected optimal point. If more ore material would have been available, the increase of confirmation runs perhaps could have approached the mean of the results to the predicted mean.

On regard to the remaining three responses, it can be observed how, as the model quality degrades, both confidence and tolerance intervals broaden in relation to the response values from the original experimental data. While predictions for the four responses could be considered as accurate enough, their tolerance intervals are

considerably widespread, which can be the explanation for the confirmation tests results falling well within range, instead of it being due to accurate predictions.

9 Conclusions

A case study was developed in this thesis for the modeling and optimization of the copper flotation process based on a Design of Experiments approach for minimum number of tests, as well as the Response Surface Methodology for the modeling and optimization of the process from the obtained laboratory results.

A total of four models were obtained, one for each of the most important responses in terms of their relevance for the rougher flotation stage of a copper-nickel concentrator. The responses modeled from the system were copper recovery, copper grade in the rougher concentrate, iron recovery and nickel recovery. The experimental design was adapted to laboratory-scale flotation tests, selecting three variables to describe each of the four models. The selected variables were pH, collector and depressant dosage; each of them acquiring five different values within a defined range of exploration in order to fit the requirements of a typical Central Composite Design.

Through the application of regression methods, quadratic models were obtained for copper recovery, grade and iron recovery; for the response of nickel recovery, the most suited model was a second degree with interactions model. Each of the obtained models present different qualities, varying in terms of the error associated to predictions based on them. The assessment of the prediction capabilities of the models was performed after optimizing the system for copper recovery and expected values of the other responses within defined ranges. This assessment consisted of performing three confirmation tests at selected optimal and constant values for the selected variables, calculating the average result for each of the responses and comparing to the tolerance intervals for each of the responses models.

The base-case values of the three variables were 10.8, 32.5 g/t and 52.5 g/t for pH, collector and depressant dosage respectively. The optimal point determined from the study resulted in a pH reduction of 0.3 units to 10.5, and collector and

depressant dosage changes to 26 g/t and 65 g/t respectively. These changes represent an alternative for the reagent combination for operating the plant with similar costs per processed ton according to average market prices for the reagents. According to the predictions, improved results in all responses could be expected in-spite of the associated uncertainty of the models.

Copper recovery, predicted to be 85% within a tolerance interval of 81.8% - 87.9% was not at the center of its prediction, but inside limits with an average value of 82.4%. For copper grade, predicted at 8.6% in a tolerance interval of 7.5% - 9.7%, the average result was 9.16%, which was highly satisfactory. Iron recovery was predicted at 6.3% in a broad tolerance interval of 1.0% - 11.6% with an average result of 6.4%, which could be improved in precision by focusing on mineralogy rather than elemental analysis. However more costly, it could be justified in order to increase the reliability of the results. Finally, nickel recovery, predicted at 30.8% in a tolerance interval of 21.4% - 40.2% averaged a result of 38.4%, quite close to the limit and unsatisfactorily due to a preference in lower values at rougher stages of copper flotation.

While all model predictions were within the given range of their tolerance intervals, only the ones for copper recovery and grade were considered as true result of a prediction. These two responses being the most important at the rougher flotation stage, the study was deemed successful to prove that Response Surface Methodology should be strongly considered as a tool in the assessment, design and troubleshooting of Outotec's customers' operations. The results of nickel and iron recovery, while falling inside their tolerance intervals, present too much error to be considered successful predictions, which, as explained in the section of Analysis of results, was due to lack of representation by the selected variables, as well as the need for mineralogical analysis of the concentrate and feedstock material.

In summary, the utilization of design of experiments and the generation of response surfaces from important process parameters allows for rapid experimentation and generation of highly valuable process data. This data that can be utilized tactically

for generation of operating set-points, change of operating strategy under different conditions or process/quality requirements and it strongly supports the efforts for continuous improvement policies if performed in a targeted and incremental way.

10 Recommendations and future work

This chapter presents a series of recommendations in order to support the continuation of the application of Response Surface Methodology for future offerings to customers by Outotec. Although the results of this thesis were rated satisfactory by the aims of this study, more work is advised in the presented areas for the improvement of the quality of studies and results presented both internally and to potential customers.

The successful future application of Response Surface Methodology for Outotec should strongly consider the inclusion of experts with sufficient knowledge in statistical analysis and the studied processes into the teams. Such knowledge would be needed to effectively design and perform screening of variables, the determination of the operating region as well as where the physical limits of the variables to study are found.

The flexibility of the methodology would allow Outotec to apply it to a wide variety of metallurgical and beneficiation processes. However, all studies should heavily rely on the pre-existent expertise and review of specific literature in order to properly interpret the behaviors and results displayed by the regression models and in order to make well informed decisions for operating strategies and prediction of results.

The use of historical plant data available through remote process monitoring as well as advanced monitoring systems such as Outotec courier® and PSI® could represent an important advantage for the implementation of optimization studies applying RSM, since it would help on the variable screening phase as well as to interpret the system responses in a well-informed way.

The application of scale-up factors would be of utmost importance before deciding to perform a plant trial with the selected optimal profile in order to assess the

quality of the study and seize the benefits derived from an optimization study. The selection of these scale-up factors should be performed by experienced professionals of the particular process from Outotec or the customer organization.

Lastly, it is advised that more case studies should be developed whenever possible in order to explore the applicability of the methodology with other process stages as well as other processes pertaining to Outotec's business within the metallurgical industry. Depending on the process stage, the type of variables would differ, as well as the amount handled and the observable gains in performance, which is the main idea behind continuous improvement policies in any industry.

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APPENDIX 1. Critical Values for the F-Distribution F(0.95). Anonymous (2013)

F-Distribution (0.95)

DF	DF Numerator														
Den.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**15**	**20**	**30**	**60**	**100**
1	161.45	199.50	215.71	224.58	230.16	233.99	236.77	238.88	240.54	241.88	245.95	248.02	250.10	252.20	253.04
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.43	19.45	19.46	19.48	19.49
3	10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.66	8.62	8.57	8.55
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.80	5.75	5.69	5.66
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.56	4.50	4.43	4.41
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.87	3.81	3.74	3.71
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.44	3.38	3.30	3.27
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	3.15	3.08	3.01	2.97
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.94	2.86	2.79	2.76
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.77	2.70	2.62	2.59
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85	2.72	2.65	2.57	2.49	2.46
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.62	2.54	2.47	2.38	2.35
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67	2.53	2.46	2.38	2.30	2.26
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.46	2.39	2.31	2.22	2.19
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.33	2.25	2.16	2.12
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.35	2.28	2.19	2.11	2.07
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.31	2.23	2.15	2.06	2.02
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.27	2.19	2.11	2.02	1.98
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.23	2.16	2.07	1.98	1.94
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.20	2.12	2.04	1.95	1.91
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37	2.32	2.18	2.10	2.01	1.92	1.88
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34	2.30	2.15	2.07	1.98	1.89	1.85
23	4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32	2.27	2.13	2.05	1.96	1.86	1.82
24	4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30	2.25	2.11	2.03	1.94	1.84	1.80
25	4.24	3.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28	2.24	2.09	2.01	1.92	1.82	1.78
26	4.23	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27	2.22	2.07	1.99	1.90	1.80	1.76
27	4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25	2.20	2.06	1.97	1.88	1.79	1.74
28	4.20	3.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24	2.19	2.04	1.96	1.87	1.77	1.73
29	4.18	3.33	2.93	2.70	2.55	2.43	2.35	2.28	2.22	2.18	2.03	1.94	1.85	1.75	1.71
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.01	1.93	1.84	1.74	1.70
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04	1.99	1.84	1.75	1.65	1.53	1.48
100	3.94	3.09	2.70	2.46	2.31	2.19	2.10	2.03	1.97	1.93	1.77	1.68	1.57	1.45	1.39
1000	3.85	3.00	2.61	2.38	2.22	2.11	2.02	1.95	1.89	1.84	1.68	1.58	1.47	1.33	1.26